Supporting Information for

A New Copper-Catalyzed Mechanism Facilitates Mild and Efficient Dehydration of Primary Amides to Nitriles Using Hydrosilanes

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1. General Information

1.1. General Reagent Information

Unless noted otherwise, reagents and substrates were purchased from commercial vendors and used as supplied. DCyPE was obtained from Aldrich and stored under inert atmosphere in the glovebox. Copper(II) acetate was purchased from Strem (amorphous powder, 97% min.) and used directly. Dimethoxymethylsilane ($(MeO)_2MeSiH$, moisture-sensitive) was purchased from TCI-America. *Caution:* Dimethoxy(methyl)silane (DMMS, CAS #16881-77-9) is listed by several vendors (TCI, Alfa Aesar) SDS or MSDS as a H318, a category 1 Causes Serious Eye Damage. Other vendors (Sigma Aldrich, Gelest) list DMMS as a H319, a category II Eye Irritant. DMMS should be handled in a well-ventilated fumehood using proper precaution as outlined for the handling of hazardous materials in "Prudent Practices in the Laboratory.[1]" At the end of the reaction either ammonium fluoride in methanol, aqueous sodium hydroxide (1 M), or aqueous hydrochloric acid (1 M) should be carefully added to the reaction mixture. This should be allowed to stir for at least 30 min or the time indicated in the detailed reaction procedure. All other reagents were purchased from Sigma Aldrich, Alfa Aesar, Strem, TCI-America, Combi-Blocks, or Matrix Scientific and were used as received. Toluene was obtained from J.T. Baker in CYCLE-TAINER® delivery kegs and purified by successive filtrations though packed columns of neutral alumina and copper(II) oxide under argon pressure; EtOAc, DCM, and hexanes used in chromatography eluents products and their derivatives were reagent grade, from Sigma-Aldrich. Flash chromatography was performed on wet-loaded, manually eluted silica columns using SiliCycle SiliaFlash® F60 silica gel (40-63 µm, 230-400 mesh, 60 Å pore diameter). Analtech Uniplate™ preparative thin-layer chromatography (TLC) plates (silica gel GF, 1000 µm, UV254 indicator, 20x20 cm) were employed in preparative TLC purifications. Standard reactions were performed in glass culture tubes with threaded ends (Fisher Scientific part #14-959-35A; oven-dried at 140 °C for 16 h prior to use) that were sealed with screw-thread caps (Kimble-Chase part #73804-15425) fitted with PTFE/silicone septa (Thermo Fisher scientific part #B799515).

1.2. General Analytical Information

^1H and ^{13}C NMR spectra were recorded using a Bruker 401 MHz spectrometer. Chemical shifts of ^1H NMR signals are referenced to the indicated residual solvent peak ($CDCl_3$, δ = 7.26 ppm) and reported in ppm relative to tetramethylsilane. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.16 ppm) and all were obtained with ^1H decoupling. $CDCl_3$ was obtained from Cambridge Isotope Laboratories. IR spectra were acquired from neat samples using a Thermo Scientific Nicolet iS5 spectrometer equipped

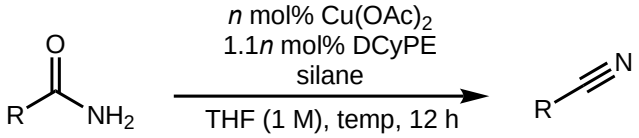
[1] "Prudent practices in the laboratory [electronic resource]: handling and management of chemical hazards / Committee on Prudent Practices in the Laboratory: An Update."; Board on Chemical Sciences and Technology, Division on Earth and Life Studies, National Research Council of the National Academics. Washington, D.C.: National Academies Press, 2011.

with an iD5 diamond laminate ATR accessory, and representative peaks are reported as wavenumbers in units of cm^{-1}. Melting points (m.p.) were obtained on a Mel-Temp capillary melting point apparatus. High-resolution mass spectrometry was performed using a Bruker Daltonics APEXIV 4.7 Tesla Fourier transform ion cyclotron resonance mass spectrometer.

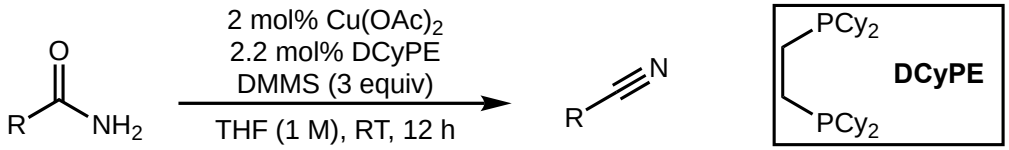
The enantiomeric excesses of products (ee) were determined by high performance liquid chromatography (HPLC). Specific columns and analytical methods are provided in the experimental details for individual compounds; the wavelengths of light used for chiral analyses are provided with the associated chromatograms. Gas Chromatography (GC) was performed using an Agilent 7890A gas chromatograph equipped with an FID detector and a J&W DB-1 column (10 mm, 0.1 mm I.D.). Analytical TLC was performed using Silicycle SilicaPlate® glass-backed extra-hard-layer TLC plates (60 Å, 250 µm thickness, 20x20 cm, UV-254 indicator) and visualization with 254 nm light.

2. Experimental Details and Characterization

2.1 Experimental Procedures for Copper-Catalyzed Dehydration of Primary Amides

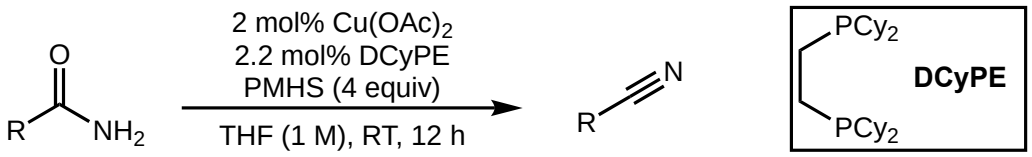


General Procedure A: Evaluation of reaction conditions on small scale (0.1 mmol). An oven-dried 1 dram vial was charged with the appropriate amide substrate (0.1 mmol, 1 equiv) and a magnetic stirring bar. The vial was transferred into a nitrogen-filled glovebox. Inside the glovebox, copper(II) acetate (n mol%), ligand (1.1n mol%), and THF (0.1 mL) were added to the reaction vessel. The solution was stirred vigorously at rt for 5 min, or homogenized using a vortexer for 1 min. While continuously stirring, the appropriate silane (2 to 4 equiv) was added dropwise to the solution using a plastic 1 mL syringe, during which time hydrogen gas evolved in some cases. After 5 min, the tube was sealed tightly with a screw cap equipped with a rubber septum (Thermo Scientific 13 mm screw cap; TEF/SIL septum, #C4015-66A) and removed from the glovebox. The reaction was stirred at roughly 750 rpm inside a fume hood at the indicated temperature 12 h. After cooling to rt, the reaction vessel was uncapped, and the reaction was quenched using saturated ammonium fluoride in methanol (1 mL), which was added **slowly** (about 1 min, **CAUTION: vigorous hydrogen gas evolution**) using a glass pipette. After stirring for 30 min at rt with the cap open, the solvent was removed with the aid of a rotary evaporator. The residue was dissolved in $CDCl_3$, and an internal standard (1,1,2,2-tetrachloroethane) was added. This mixture was transferred to an NMR tube and the yield was determined using ^1H NMR.



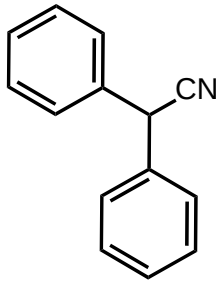
General Procedure B: 1 mmol scale dehydration of primary amides using DMMS. An oven-dried screw-cap reaction tube (13 x 100 mm), Fisher brand #1495935C) was charged with the appropriate amide substrate (1 mmol, 1 equiv) and a magnetic stirring bar. The tube was transferred into a nitrogen-filled glovebox. Inside the glovebox, copper(II) acetate (3.6 mg, 0.02 mmol, 0.02 equiv), 1,2-bis(dicyclohexylphosphino)ethane (9.3 mg, 0.022 mmol, 0.022 equiv), and THF (1.0 mL) were added to the reaction vessel. The solution was stirred vigorously at rt for 5 min, during which a dark blue color developed. While continuously stirring, dimethoxy(methyl)silane (0.375 mL, 3.0 mmol, 3.0 equiv) was added dropwise to the solution using a plastic 1 mL syringe, during which time hydrogen gas was evolved. After 5 min, the tube was sealed tightly with a screw cap equipped with a rubber septum (Thermo Scientific 13 mm screw cap; TEF/SIL septum, #C4015-66A) and removed from

the glovebox. The reaction was stirred at roughly 750 rpm inside a fume hood at rt for 12 h. At this point, the reaction vessel was uncapped, and the reaction was quenched using saturated ammonium fluoride in methanol (5 mL), which was added **slowly** (about 1 min, **CAUTION: vigorous hydrogen gas evolution**) using a glass pipette. After stirring for 30 min at rt with the cap open, the reaction was transferred to a 20 mL scintillation vial using EtOAc (10 mL). The solvent was removed with the aid of a rotary evaporator, and the residue was suspended in 15 mL EtOAc and stirred vigorously for 10 min. The solution was eluted through a short plug of Celite (~10 g) with additional EtOAc. After concentration of the filtrate by with the aid of a rotary evaporator, the residue was purified by column chromatography with the aid of a Biotage Isolera instrument.



General Procedure C: 1 mmol scale dehydration of primary amides using PMHS. An oven-dried screw-cap reaction tube (13 x 100 mm), Fisher brand #1495935C) was charged with the appropriate amide substrate (1 mmol, 1 equiv) and a magnetic stirring bar. The tube was transferred into a nitrogen-filled glovebox. Inside the glovebox, copper(II) acetate (3.6 mg, 0.02 mmol, 0.02 equiv), 1,2-bis(dicyclohexylphosphino)ethane (9.3 mg, 0.022 mmol, 0.022 equiv), and THF (1.0 mL) were added to the reaction vessel. The solution was stirred vigorously at rt for 5 min, during which a dark blue color developed. While continuously stirring, poly(methylhydrosiloxane) (PMHS, Aldrich #176206, TMS-terminated, average Mn = 1700–3200, 0.240 mL, 4.0 mmol hydride, 4 equiv) was added dropwise to the solution using a plastic 1 mL syringe, during which time hydrogen gas was evolved. After 5 min, the tube was sealed tightly with a screw cap equipped with a rubber septum (Thermo Scientific 13 mm screw cap; TEF/SIL septum, #C4015-66A) and removed from the glovebox. The reaction was stirred at roughly 750 rpm inside a fume hood at rt for 12 h. At this point, the reaction vessel was uncapped, and the reaction was quenched using saturated ammonium fluoride in methanol (5 mL), which was added **slowly** (about 1 min, **CAUTION: vigorous hydrogen gas evolution**) using a glass pipette. After stirring for 30 min at rt with the cap open, the reaction was transferred to a 20 mL scintillation vial using EtOAc (10 mL). The solvent was removed with the aid of a rotary evaporator, and the residue was suspended in 15 mL EtOAc and stirred vigorously for 10 min. The solution was eluted through a short plug of Celite (~10 g) with additional EtOAc. After concentration of the filtrate with the aid of a rotary evaporator, the residue was purified by column chromatography with the aid of a Biotage Isolera instrument.

2.2 Specific Reaction Conditions and Characterization for Nitrile Products



2,2-diphenylacetonitrile (2a)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (211 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 20% EtOAc in hexanes) to afford the title compound as a white solid.

Run 1: 182 mg, 94% yield
Run 2: 175 mg, 90% yield

A third run was performed following General Procedure C. $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), PMHS (160 μL, 4.0 mmol), THF (1.0 mL), and the corresponding primary amide (211 mg, 1.0 mmol) were used. The same purification conditions as above were used.

Run 3: 174 mg, 90% yield

A fourth run at gram-scale (25 mmol) was performed using Procedure D, see below.

Run 4: 4.82 g, 99% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.32 (m, 10H), 5.15 (s, 1H)

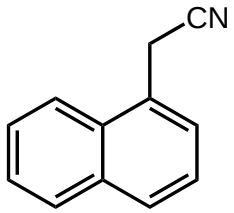
^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 129.3, 128.4, 127.9, 119.8, 42.7

These spectroscopic data precisely match those previously reported in the literature.[2] For further characterization, please see the reference cited.

Procedure D: 25 mmol scale dehydration of 2,2-diphenylacetamide using PMHS. An oven-dried 100 mL one-neck round-bottom flask was cooled to rt under a stream of dry nitrogen gas, supplied by an inert gas manifold. The flask was charged with 2,2-diphenylacetamide (5.28 g, 25 mmol, 1 equiv), copper(II) acetate (45.4 mg, 0.25 mmol, 0.01 equiv), bis(dicyclohexylphosphino)ethane (0.011 mg, 0.275 mmol, 0.011 equiv),

[2] Wang, J.; Masui, Y.; Onaka, M. *ACS Catal*. **2011**, 1, 446.

and a magnetic stirring bar. The flask was sealed with a rubber septum, and a needle connected to the inert gas manifold was inserted through this septum. The flask was placed under vacuum and refilled with dry nitrogen. This process was repeated a total of three times, and the flask was left under a slight positive pressure of nitrogen supplied through the manifold. THF (25 mL) was added and the mixture was stirred for 5 min until a deep blue colored solution formed. Using a 12 mL plastic syringe with a needle attached, poly(methylhydrosiloxane) (PMHS, Aldrich #176206, TMS-terminated, average Mn = 1700–3200, 6.0 mL, 100 mmol hydride, 4 equiv) was added slowly over 5 min (**CAUTION: vigorous hydrogen gas evolution! Must be vented to inert gas manifold!**) The reaction was allowed to stir at rt for 12 h. At this point, the septum was carefully removed, and the reaction was quenched by slowly pouring into a 500 mL Erlenmeyer flask containing saturated ammonium fluoride in methanol (200 mL, **CAUTION: vigorous hydrogen gas evolution! Must be performed in a well-ventilated fume hood away from ignition sources or flammable solvents!)**. After stirring for 30 min at rt, the mixture was concentrated with the aid of a rotary evaporator. The residue was suspended in EtOAc (300 mL), and filtered through a short plug of Celite (~200 g) with additional EtOAc (300 mL). The combined filtrate was washed sequentially with water (2 x 200 mL) and brine (200 mL), then dried over sodium sulfate and subjected to gravity filtration. The filtrate was concentrated with the aid of a rotary evaporator to yield the crude product as a white, semi-crystalline solid. This crude product was purified by recrystallization from hot acetone to yield a colorless, crystalline solid, with spectroscopic properties precisely matching those reported above (4.82 g, 99% yield).



2-(naphthalen-1-yl)acetonitrile (2b)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (167 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 15% EtOAc in hexanes) to afford the title compound as yellow, viscous liquid.

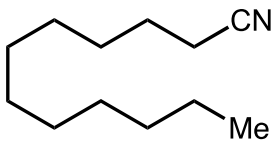
Run 1: 140 mg, 94% yield
Run 2: 144 mg, 96% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.86-7.81 (m, 2H), 7.62-7.56 (m, 3H), 7.45 (t, *J* = 8.0 Hz, 1H), 4.04 (s, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 130.7, 129.1, 129.0, 127.0, 126.4, 126.3, 125.8, 125.5, 122.4, 117.8, 21.6

These spectroscopic data precisely match those previously reported in the literature.[3] For further characterization, please see the reference cited.

[3] Shang, R.; Ji, D.-S.; Chu, L.; Fu, Y.; Liu, L. *Angew. Chem., Int. Ed.* **2011**, 50, 4470.



Dodecanenitrile (2c)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), **toluene instead of THF** (1.0 mL), and the corresponding primary amide (199 mg, 1.0 mmol) were used. The reaction mixture was purified using a short plug of silica (around 20 g). The column was first eluted using hexanes (5 mL) to remove silane impurities. Then, 10% EtOAc/hexanes (10 mL) was used to elute the title compound as a pure, white solid.

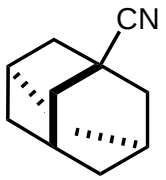
Run 1: 174 mg, 96% yield
Run 2: 167 mg, 92% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.34-2.29 (m, 2H), 1.67-1.59 (m, 2H), 1.45-1.39 (m, 2H), 1.31-1.24 (m, 14H), 0.88-0.84 (m, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 120.0, 32.0, 29.7, 29.6, 29.4, 28.9, 28.8, 25.5, 22.8, 17.2, 17.2, 14.2

These spectroscopic data precisely match those previously reported in the literature.[4] For further characterization, please see the reference cited.

[4] Bencivenni, G.; Lanza, T.; Leardini, R.; Minozzi, M.; Nanni, D.; Spagnolo, P.; Zanardi, G. *J. Org. Chem.* **2008**, 73, 4721.



Adamantane-1-carbonitrile (2d)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (179 mg, 1.0 mmol) were used. Instead of running the reaction at rt, the reaction flask was partially submerged in a 50 °C oil bath after addition of silane. After 12 h, the flask was cooled to rt before the quench. The reaction mixture was purified using a short plug of silica (around 20 g). The column was first eluted using hexanes (5 mL) to remove silane impurities. Then, 20% EtOAc/hexanes (20 mL) was used to elute the title compound as a pure, white solid.

Run 1: 141 mg, 88% yield
Run 2: 139 mg, 86% yield

A third run was performed following General Procedure C. $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), PMHS (160 μL, 4.0 mmol), THF (1.0 mL), and the corresponding primary amide (179 mg, 1.0 mmol) were used. Instead of running the reaction at rt, the reaction flask was partially submerged in a 50 °C oil bath after addition of silane. After 12 h, the flask was cooled to rt before the quench. The same purification conditions as above were used.

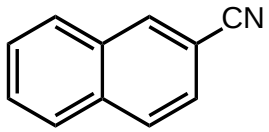
Run 3: 135 mg, 84% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03 (s, 9H), 1.76-1.69 (m, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 125.4, 40.1, 35.9, 30.3, 27.2

These spectroscopic data precisely match those previously reported in the literature.[5] For further characterization, please see the reference cited.

[5] Bindl, M., Stade, R., Heilmann, E. K., Picot, A., Goddard, R., and Fürstner, A. *J. Am. Chem. Soc.* **2009**, 131, 9468.



2-naphthonitrile (2e)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (171 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to XX % DCM in hexanes) to afford the title compound as a clear oil.

Run 1: 144 mg, 94% yield
Run 2: 143 mg, 94% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.89-7.84 (m, 3H), 7.65-7.56 (m, 3H)

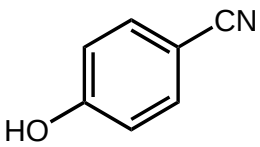
^{13}C NMR (100 MHz, $CDCl_3$): δ 134.7, 134.2, 132.2, 129.2, 129.1, 128.4, 128.1, 127.7, 126.3, 119.3, 109.4

A third run was performed following General Procedure C. $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), PMHS (160 μL, 4.0 mmol), THF (1.0 mL), and the corresponding primary amide (171 mg, 1.0 mmol) were used. The same purification conditions as above were used.

Run 3: 148 mg, 96% yield

These spectroscopic data precisely match those previously reported in the literature.[6] For further characterization, please see the reference cited.

[6] Zhou, W.; Xu, J.; Zhang, L.; Jiao, N. *Org. Lett.* **2010**, 12, 2888.



4-hydroxybenzonitrile (2f)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ **(500 µL, 4.0 mmol)**, THF (1.0 mL), and the corresponding primary amide (137 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 45% EtOAc in hexanes) to afford the title compound as a white solid. The compound co-elutes with a small amount (4%) of 4-hydroxybenzaldehyde under these conditions; we were not able to separate this mixture easily by column chromatography.

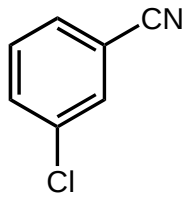
Run 1: 98 mg, 80% yield
Run 2: 97 mg, 80% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.52 (s, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 134.5, 119.4, 116.6, 103.4

These spectroscopic data precisely match those previously reported in the literature.[7] For further characterization, please see the reference cited.

[7] Yang, H.; Li, Y.; Jiang, M.; Wang, J.; Fu, H. *Chem.–Eur. J.* **2011**, 17, 5652.



3-chlorobenzonitrile (2g)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (156 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 10% EtOAc in hexanes) to afford the title compound as a white solid. The compound co-elutes with a small amount (4%) of 3-chlorobenzaldehyde under these conditions; we were not able to separate this mixture easily by column chromatography.

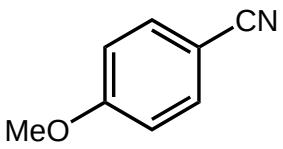
Run 1: 111 mg, 80% yield
Run 2: 112 mg, 81% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 1H), 7.53-7.46 (m, 1H), 7.40-7.35 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4, 133.4, 132.1, 130.6, 130.4, 117.6, 114.13

These spectroscopic data precisely match those previously reported in the literature.[8] For further characterization, please see the reference cited.

[8] Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, 50, 519.



4-methoxybenzonitrile (2h)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (151 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 50% DCM in hexanes) to afford the title compound as a white solid.

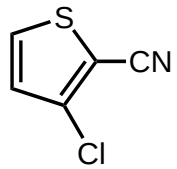
Run 1: 113 mg, 85% yield
Run 2: 114 mg, 86% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 7.0, 2.2 Hz, 2H), 6.95 (dd, *J* = 6.9, 2.3 Hz, 2H), 3.85 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 134.2, 119.4, 114.9, 104.2, 55.7

These spectroscopic data precisely match those previously reported in the literature.[9] For further characterization, please see the reference cited.

[9] Bindl, M., Stade, R., Heilmann, E. K., Picot, A., Goddard, R., and Fürstner, A. *J. Am. Chem. Soc.* **2009**, 131, 9468.



3-chlorothiophene-2-carbonitrile (2i)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (162 mg, 1.0 mmol) were used. The product was purified by column chromatography (gradient elution, hexanes to 30% DCM in hexanes) to obtain a white solid.

Initially, ^1H NMR of the crude mixture indicates the formation of a small amount (9%) of 3-chlorothiophene-2-carbaldehyde, most of which can be removed under the indicated column chromatography conditions (<3% remaining).

Run 1: 96 mg, 67% yield
Run 2: 100 mg, 70% yield

A third run was performed following General Procedure C. $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), PMHS (160 μL, 4.0 mmol), THF (1.0 mL), and the corresponding primary amide (171 mg, 1.0 mmol) were used. The same purification conditions as above were used.

Run 3: 94 mg, 65% yield

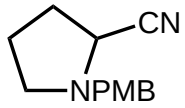
^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 5.4 Hz, 1H), 7.06 (d, *J* = 5.4 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2, 132.6, 128.3, 112.0, 106.0

m.p. (uncorrected, capillary): 63 °C

These spectroscopic data precisely match those previously reported in the literature.[10] For further characterization, please see the reference cited.

[10] El Kassmi, A.; Fache, F.; Lemaire, M. *Synth. Commun.* **1994**, *24*, 95.



1-(4-methoxybenzyl)pyrrolidine-2-carbonitrile (2j)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (243 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 25% EtOAc in hexanes) to afford the title compound as a yellow oil.

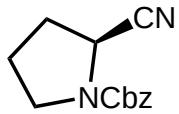
Run 1: 181 mg, 80% yield
Run 2: 186 mg, 83% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.80 (d, *J* = 12.7 Hz, 1H), 3.75 (s, 3H), 3.62 (d, *J* = 7.4 Hz, 1H), 3.58 (d, *J* = 12.8 Hz, 1H), 2.92-2.88 (m, 1H), 2.55-2.50 (m, 1H), 2.20-1.84 (m, 4H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 130.2, 130.0, 118.1, 114.0, 56.0, 55.4, 53.2, 51.2, 29.6, 22.0

These spectroscopic data precisely match those previously reported in the literature.[11] For further characterization, please see the reference cited.

[11] Das, D.; Richers, M. T.; Ma, L.; Seidel, D. *Org. Lett.* **2011**, 13, 6584.



Benzyl (*S*)-2-cyanopyrrolidine-1-carboxylate (2k)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (248 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 60% EtOAc in hexanes) to afford the title compound as a yellow oil.

Run 1: 213 mg, 93% yield
Run 2: 201 mg, 88% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.30 (m, 5H), 5.22-5.15 (m, 2H), 4.62-4.54 (m, 2H) 3.58-3.41 (m, 2H), 2.27-2.05 (m, 4H)

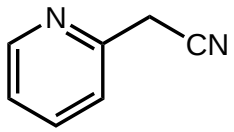
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4, 153.7, 136.2, 136.1, 128.7, 128.4, 128.3, 119.0, 118.4, 67.9, 67.8, 47.6, 47.1, 46.5, 46.1, 31.9, 30.9, 24.8, 23.9

These spectroscopic data precisely match those previously reported in the literature.[12] For further characterization, please see the reference cited.

Determination of Enantiospecificity

Enantiopure (>99% ee) starting material was used, and the enantiomeric excess of the product was obtained according to conditions reported in the literature for CSP-HPLC analysis of **2k**[12] (Daicel Chiralpak AD-H column, hexane/isopropanol 90:10, 1.0 mL/min flow rate, 210 and 254 nm detection). Retention times: t_R = 14.2 (not detected), t_S = 19.5 min (>99.9%).

[12] Aureggi, V.; Franckevicius, V.; Kitching, M.; Ley, S.; Longbottom, D.; Oelke, A.; Sedelmeier, G. *Org. Synth.* **2008**, 85, 72.



2-(pyridin-2-yl)acetonitrile (2l)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (136 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 55% EtOAc in hexanes) to afford the title compound as a brown liquid.

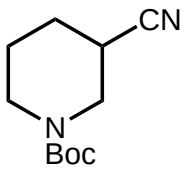
Run 1: 95 mg, 81% yield
Run 2: 94 mg, 80% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* = 5.0 Hz, 1H), 7.76 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 6.3 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 150.1, 137.6, 123.2, 122.4, 117.1, 26.8

These spectroscopic data precisely match those previously reported in the literature.[13] For further characterization, please see the reference cited.

[13] Velcicky, J.; Soicke, A.; Steiner, R.; Schmalz, H.-G. *J. Am. Chem. Soc.* **2011**, 133, 6948.



***tert*-butyl 3-cyanopiperidine-1-carboxylate (2m)**

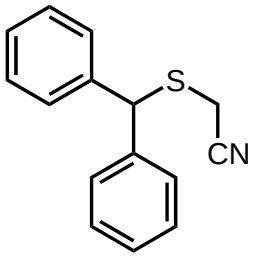
Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (228 mg, 1.0 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 30% EtOAc in hexanes) to afford the title compound as a yellow oil.

Run 1: 203 mg, 97% yield
Run 2: 197 mg, 94% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.69-3.47 (m, 4H), 2.66 (m, 1H),

^{13}C NMR (100 MHz, $CDCl_3$): δ 120.2, 80.6, 46.2, 43.6, 28.5, 28.4, 28.1, 27.6, 23.2

IR (neat): 2977, 2925, 2858, 2240, 1682, 1411



2-(benzhydrylthio)acetonitrile (2n)

Following General Procedure B, $Cu(OAc)_2$ (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), $(MeO)_2MeSiH$ (375 μL, 3.0 mmol), THF (1.0 mL), and the corresponding primary amide (128 mg, 0.5 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 30% EtOAc in hexanes) to afford the title compound as a white solid.

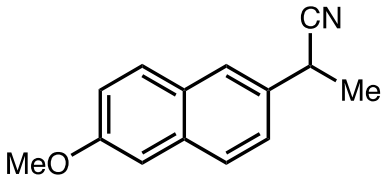
Run 1: 92 mg, 77% yield
Run 2: 86 mg, 74% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.4 Hz, 4H), 7.36 (t, *J* = 7.2 Hz, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 5.44 (s, 1H), 3.08 (s, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 129.1, 128.6, 128.2, 116.4, 54.4, 17.6

These spectroscopic data precisely match those previously reported in the literature.[14] For further characterization, please see the reference cited.

[14] Akopova, A. R.; Morkovnik, A. S.; Khrustalev, V. N.; Bicherov, A. V. *Russ. Chem. Bull.* **2013**, 62, 1164



2-(6-methoxynaphthalen-2-yl)propanenitrile (2o)

Following General Procedure B, $Cu(OAc)_2$ (1.8 mg, 0.01 mmol), DCyPE (4.7 mg, 0.011 mmol), $(MeO)_2MeSiH$ (187 μL, 1.5 mmol), THF (1.0 mL), and the corresponding primary amide (115 mg, 0.5 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 35% EtOAc in hexanes) to afford the title compound as a white solid.

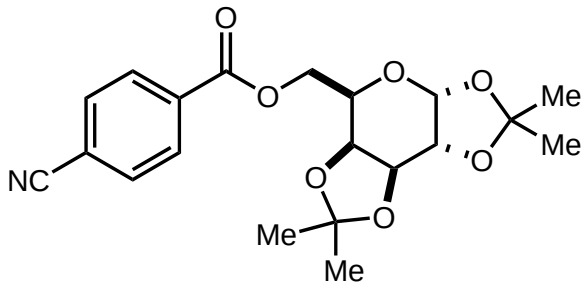
Run 1: 95 mg, 91% yield
Run 2: 106 mg, 94% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 8.9 Hz, 3H), 7.39 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.19 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 4.03 (q, *J* = 7.3 Hz, 1H), 3.93 (s, 3H), 1.71 (d, *J* = 7.3 Hz, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 134.2, 132.2, 129.5, 128.9, 128.1, 125.6, 125.1, 121.9, 119.7, 105.8, 55.5, 31.4, 21.6

These spectroscopic data precisely match those previously reported in the literature.[15] For further characterization, please see the reference cited.

[15] Wu, L.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, 127, 15824



Galactose derivative 2p

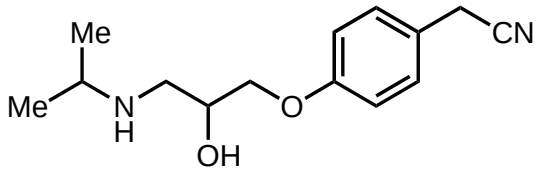
Following General Procedure B, $Cu(OAc)_2$ (1.8 mg, 0.01 mmol), DCyPE (4.7 mg, 0.011 mmol), $(MeO)_2MeSiH$ (187 μL, 1.5 mmol), THF (1.0 mL), and the corresponding primary amide (204 mg, 0.5 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 20% EtOAc in hexanes) to afford the title compound as a yellow oil.

Run 1: 173 mg, 89% yield
Run 2: 175 mg, 90% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 5.54 (d, *J* = 5.0 Hz, 1H), 4.65 (dd, *J* = 7.9, 2.4 Hz, 1H), 4.52 (dd, *J* = 11.6, 4.5 Hz, 1H), 4.43 (dd, *J* = 11.6, 7.8 Hz, 1H), 4.33 (m, 1H), 4.28 (dd, *J* = 7.9, 1.8 Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 134.0, 132.3, 130.3, 118.1, 116.5, 109.9, 108.9, 96.4, 71.2, 70.8, 70.6, 66.1, 64.8, 26.1 (2C), 25.0, 24.6

IR (neat): 2989, 2936, 2232, 1725, 1274, 1067 cm^{-1}



Atenolol derivative 2q

Following General Procedure B, $Cu(OAc)_2$ (1.8 mg, 0.01 mmol), DCyPE (4.7 mg, 0.011 mmol), $(MeO)_2MeSiH$ (**310 µL, 2.5 mmol**), THF (1.0 mL), and the corresponding primary amide (133 mg, 0.5 mmol) were used. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 10% acetone in hexanes) to afford the title compound as a yellow solid.

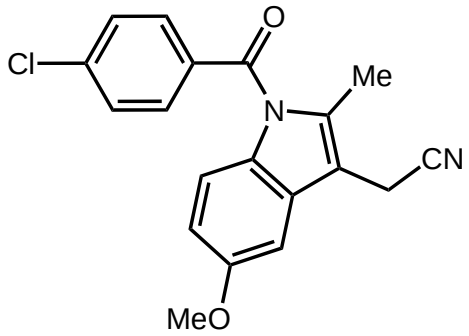
Run 1: 119 mg, 96% yield
Run 2: 113 mg, 91% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.07-4.02 (m, 1H), 3.97-3.94 (m, 2H), 3.67 (s, 2H), 3.00-2.83 (m, 4H), 2.76-2.71 (m, 1H), 1.11 (d, *J* = 6.2 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 129.2, 122.3, 118.3, 115.3, 70.8, 68.3, 49.3, 49.2, 23.0, 22.9

IR (neat): 3277, 3119, 2964, 2927, 2246, 1512

m.p. (uncorrected, capillary): 139 °C



Indomethacin derivative 2r

Following General Procedure B, $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), DCyPE (23.2 mg, 0.055 mmol), $(MeO)_2MeSiH$ (187 μL, 1.5 mmol), **1,4-dioxane (2.0 mL)**, and the corresponding primary amide (178 mg, 0.5 mmol) were used. Instead of running the reaction at rt, the reaction flask was partially submerged in a 40 °C oil bath after addition of silane. After **40 min**, the flask was cooled to rt before the quench. The reaction mixture was purified by flash column chromatography (gradient elution, hexanes to 30% EtOAc in hexanes) to afford the title compound as a yellow solid.

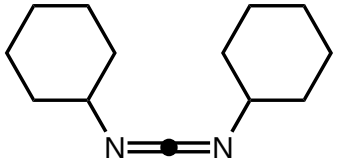
Run 1: 91 mg, 54% yield
Run 2: 91 mg, 54% yield

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 2H), 2.43 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 156.4, 139.9, 136.1, 133.5, 131.4, 130.8, 129.4, 129.2, 128.8, 128.4, 115.3, 112.6, 108.2, 100.6, 55.9, 13.3

IR (neat): 3100, 2910, 2246, 1681, 1349, 1324

m.p. (uncorrected, capillary): 121 °C



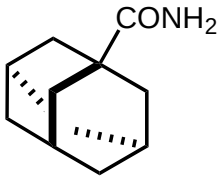
***N,N*-dicyclohexylcarbodiimide (2s)**

Inside a nitrogen-filled glovebox, an oven-dried 1 dram vial was charged with *N,N'*-dicyclohexylurea (56.1 mg, 0.25 mmol, 1 equiv) and a magnetic stirring bar. The vial was further charged with copper(II) acetate (2.3 mg, 0.0125 mmol, 0.05 equiv), 1,2-bis(dicyclohexlyphosphino)ethane (6.3 mg, 0.015 mmol, 0.06 equiv), and THF (0.25 mL). The solution was vigorously stirred at rt for 5 min, during which a dark blue color developed. While continuously stirring, dimethoxy(methyl)silane (0.087 mL, 0.7 mmol, 2.5 equiv) was added dropwise to the solution using a glass 100 μL syringe, during which time hydrogen gas was evolved. After 5 min, the tube was sealed tightly with a screw cap equipped with a rubber septum (Thermo Scientific 13 mm screw cap; TEF/SIL septum, #C4015-66A) and removed from the glovebox. The tube was partially submerged in a 70 ^{o}C oil bath and the reaction mixture was stirred for 24 h. Dodecane (56.8 μL, .25 mmol, 1 equiv), an internal standard, was added via a glass 100 μL syringe. An aliquot of this mixture was diluted with ethyl acetate and analyzed by gas chromatography (GC). This analysis was performed on a Hewlett-Packard 6890 GC instrument with a flame ionization detector using 25 m × 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. The method used for quantification of the product is: (i) 70 °C oven temperature upon injection, (ii) hold at 70 °C for 2 min, (iii) increase the temperature to 250 °C for >4 min, (iv) hold at 250 °C for 2 min. The desired product was detected at a retention time of 4.21 min, showing **74% yield**, calibrated to dodecane internal standard using authentic product obtained from Sigma-Aldrich. The remaining reaction contents were quenched using saturated ammonium fluoride in methanol (2 mL), which was added **slowly** (about 1 min, **CAUTION: vigorous hydrogen gas evolution**) using a glass pipette.

2.3 Synthesis of Primary Amides

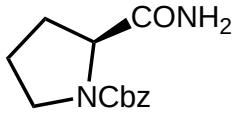
General Procedure E: An oven-dried 250 mL round-bottom flask was equipped with a magnetic stirring bar and charged with acid (15 mmol, 1.0 equiv) and dry THF (50 mL). The flask was then purged with Ar for 5 min, at which 1,1′-carbonyldiimidazole (18 mmol, 1.2 equiv) was added slowly. The reaction mixture was stirred at rt for 1 hour under Ar. After cooling to 0 °C, aq. NH_3 (7.0 mL) was added dropwise, and the reaction mixture was stirred at rt. After 4 hours, solvent was removed *in vacuo*, and the crude product was washed with 1 M NaOH and brine and was extracted with EtOAc. The organic phase was dried with sodium sulfate, and the solvent was removed *in vacuo* to afford the desired primary amide.

General Procedure F: An oven-dried 250 mL round-bottom flask was equipped with a magnetic stirring bar and charged with acid (1.0 equiv) and dry DCM (3 mL/mmol acid). The flask was then purged with Ar for 5 min. Under Ar, oxalyl chloride (1.05 equiv) was added dropwise at 0 °C. The reaction mixture was stirred at rt for 1 hour, at which the solvent was removed *in vacuo*. The crude mixture was re-dissolved into dry THF (1 mL/mmol), and aq. NH_3 (0.5 mL/mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 1 hour. Solvent was removed *in vacuo*, and the crude product was washed with 1M NaOH and brine and was extracted with EtOAc. The primary amide was purified by recrystallization from EtOAc.



Adamantane-1-carboxamide

Following General Procedure E, 1-adamantanecarboxylic acid (2.70 g, 15 mmol), 1,1′-carbonyldiimidazole (2.92 g, 18 mmol), sodium sulfate (1.00 g), and dry THF (50 mL) were used. The title compound was obtained as a white solid (2.31 g, 86% yield) with spectral properties matching those previously reported in the literature.[16]

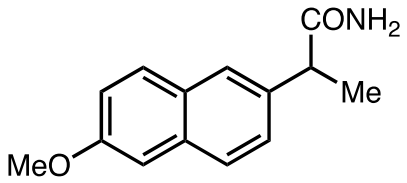


(*S*)-2-Amido-pyrrolidine-1-carboxylic acid benzyl ester

Following General Procedure F, Cbz-l-proline (3.74 g, 15 mmol), oxalyl chloride (1.35 mL, 1.05 mmol), aq. NH_3 (7.5 mL), dry DCM (45 mL) and dry THF (10 mL) were used.

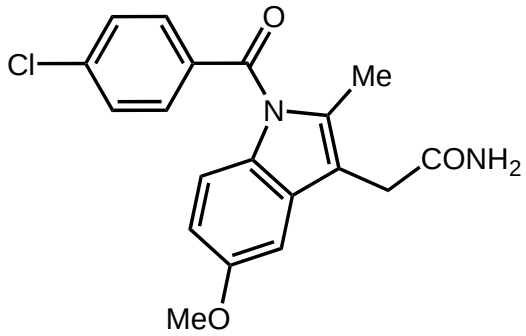
[16] Ohmura, R.; Takahata, M.; Togo, H. *Tetrahedron Lett.* **2010**, 51, 4378

The title compound was obtained as a white solid (3.45 g, 99% yield) with spectral properties matching those previously reported in the literature.[17]



2-(6-methoxynaphthalen-2-yl)propanamide

Following General Procedure F, naproxen (2.30 g, 10 mmol), oxalyl chloride (0.90 mL, 1.05 mmol), aq. NH_3 (5 mL), dry DCM (30 mL) and dry THF (10 mL) were used. The title compound was obtained as a white solid (1.56 g, 74% yield) with spectral properties matching those previously reported in the literature.[18]

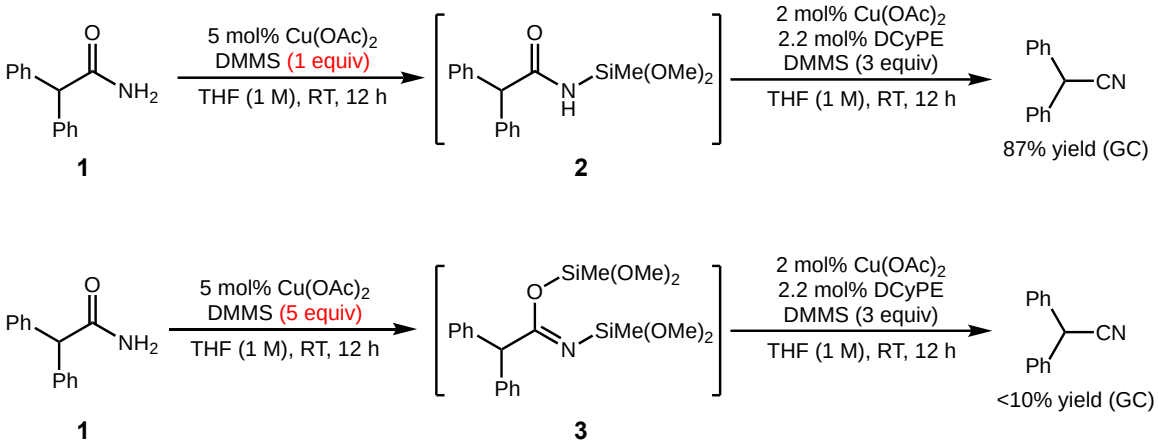


2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetamide

Following General Procedure F, Indomethacin (3.58 g, 10 mmol), oxalyl chloride (0.90 mL, 1.05 mmol), aq. NH_3 (5 mL), dry DCM (30 mL) and dry THF (10 mL) were used. The title compound was obtained as a yellow solid (3.38 g, 99% yield) with spectral properties matching those previously reported in the literature.[19]

[17] Aureggi, V.; Franckevicius, V.; Kitching, M. O.; Ley, S. V.; Longbottom, D. A.; Oelke, A. J.; Sedelmeier, G. *Org. Synth.* **2008**, 85, 72.
[18] Wojkielewicz, A.; Lotowski, Z.; Morzycki, J. W. *Synlett* **2015**, 26, 2288.
[19] Kalgutkar, A. S.; Marnett, A. B.; Crews, B. C.; Remmel, R. P.; Marnett, L. J. *J. Med. Chem.* **2000**, 43, 2860−2870.

3. Mechanistic Experiments



***In situ* generation of 2, and subsequent dehydration reaction:** An oven-dried 1 dram vial was charged with 2,2-diphenylacetamide (21.1 mg, 0.1 mmol, 1 equiv) and a magnetic stirring bar. The vial was transferred into a nitrogen-filled glovebox. Inside the glovebox, copper(II) acetate (0.9 mg, 0.005 mmol, 0.05 equiv) and THF (0.1 mL) were added to the reaction vessel. Dimethoxy(methyl)silane (12 µL, 0.1 mmol, 1 equiv) was added directly into the solution using a 50 µL glass syringe, and the vial was capped tightly. While still inside the glovebox, the mixture was stirred vigorously for 12 h, during which time the solution acquired a dark brown color. Into a separate oven-dried vial, copper(II) acetate (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), THF (1 mL), and dimethoxy(methyl)silane (375 µL, 3.0 mmol) were sequentially added. The contents of this second vial were mixed thoroughly using a vortexer for 1 min, during which a yellow-orange color should develop. 138 µL of this second solution was added into the first vial using a 1 mL plastic syringe. The first vial was capped tightly and removed from the glovebox. The reaction mixture was stirred vigorously for 12 h. At this point, the reaction vessel was uncapped, and the reaction was quenched using saturated ammonium fluoride in methanol (1 mL), which was added **slowly** (about 1 min, **CAUTION: vigorous hydrogen gas evolution**) using a glass pipette. Dodecane (56.8 µL, .25 mmol, 1 equiv), an internal standard, was added via a glass 100 µL syringe. An aliquot of this mixture was diluted with ethyl acetate and analyzed by gas chromatography (GC). This analysis was performed on a Hewlett-Packard 6890 GC instrument with a flame ionization detector using 25 m × 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. The method used for quantification of the product is: (i) 70 °C oven temperature upon injection, (ii) hold at 70 °C for 2 min, (iii) increase the temperature to 250 °C for >4 min, (iv) hold at 250 °C for 2 min. The desired product was detected at a retention time of 2.47 min, showing **87% yield**, calibrated to dodecane internal standard using authentic product obtained from Sigma-Aldrich.

***In situ* generation of 3, and attempted subsequent dehydration reaction:** An oven-dried 1 dram vial was charged with 2,2-diphenylacetamide (21.1 mg, 0.1 mmol, 1 equiv) and a magnetic stirring bar. The vial was transferred into a nitrogen-filled glovebox. Inside the glovebox, copper(II) acetate (0.9 mg, 0.005 mmol, 0.05 equiv) and THF (0.1

mL) were added to the reaction vessel. Dimethoxy(methyl)silane (61 μL, 0.5 mmol, 5 equiv) was added directly into the solution using a 50 μL glass syringe, and the vial was capped tightly. While still inside the glovebox, the mixture was stirred vigorously for 12 h, during which time the solution acquired a dark brown color. Into a separate oven-dried vial, copper(II) acetate (3.6 mg, 0.02 mmol), DCyPE (9.3 mg, 0.022 mmol), THF (1 mL), and dimethoxy(methyl)silane (375 μL, 3.0 mmol) were sequentially added. The contents of this second vial were mixed thoroughly using a vortexer for 1 min, during which a yellow-orange color should develop. 138 μL of this second solution was added into the first vial using a 1 mL plastic syringe. The first vial was capped tightly and removed from the glovebox. The reaction mixture was stirred vigorously for 12 h. At this point, the reaction vessel was uncapped, and the reaction was quenched using saturated ammonium fluoride in methanol (1 mL), which was added **slowly** (about 1 min, **CAUTION: vigorous hydrogen gas evolution**) using a glass pipette. Dodecane (56.8 μL, .25 mmol, 1 equiv), an internal standard, was added via a glass 100 μL syringe. An aliquot of this mixture was diluted with ethyl acetate and analyzed by gas chromatography (GC). This analysis was performed on a Hewlett-Packard 6890 GC instrument with a flame ionization detector using 25 m × 0.20 mm capillary column with cross-linked methyl siloxane as a stationary phase. The method used for quantification of the product is: (i) 70 °C oven temperature upon injection, (ii) hold at 70 °C for 2 min, (iii) increase the temperature to 250 °C for >4 min, (iv) hold at 250 °C for 2 min. The desired product was detected in trace quantity at a retention time of 2.47 min, showing **<10% yield**, calibrated to dodecane internal standard using authentic product obtained from Sigma-Aldrich. The starting material was detected at a retention time of 3.81 min, showing **92% recovery**, calibrated to dodecane internal standard using pure starting material.

4. Computational Details

All reported calculations were performed using the ORCA software[20] or GAUSSIAN 03.[21] Images of the 3D structures were rendered using CYLView.[22] The geometry of all reactants and transition states were optimized using the B3LYP[23,24] functional in the gas phase. In these geometry optimizations, a mixed basis set of SDD[25] for Cu and 6-31G(d)[26] for all other atoms was used. Ground and transition state geometries were validated by vibrational analysis at the same level, showing zero and one imaginary frequencies respectively. Single point energies were calculated using the M06[27] functional on a mixed basis set of SDD[28] for Cu and 6-311+G(2d,p) for all other atoms. In these energy calculations, the SMD solvation model[29] with THF as solvent was applied. The reported Gibbs free energies and enthalpies include zero-point and thermal corrections calculated at 298 K using B3LYP/SDD-6-31G(d).

Elimination from Disilyl Imidate

We modeled the thermal 1,2-elimination process from a disilyl imidate derived from acetamide and DMMS. This process is anticipated to have a high barrier based on previous studies (for instance, see refs. 6c, 6d, 6g, 6h, 6p in the manuscript). Indeed, the barrier for elimination from **S1** is predicted to be too high to be surmountable at ambient temperature (+37.0 kcal/mol).

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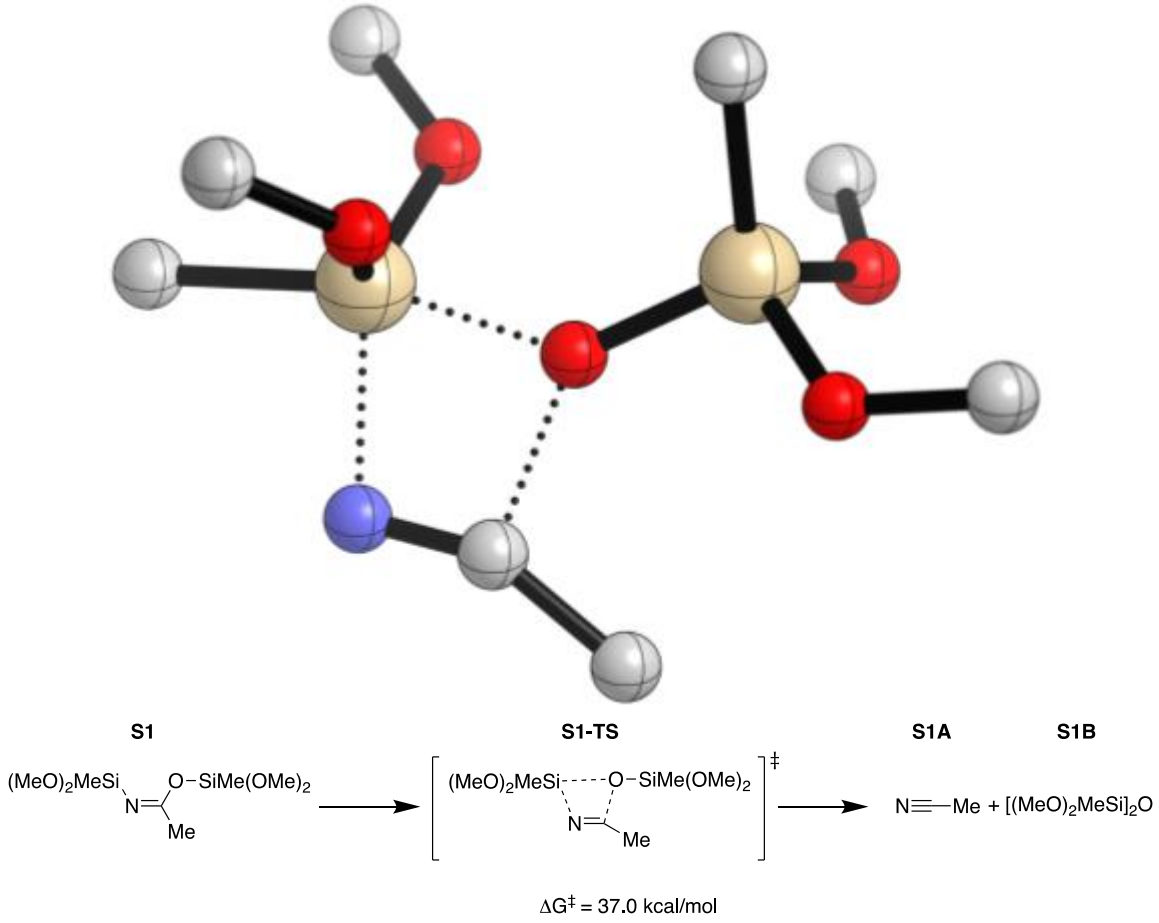
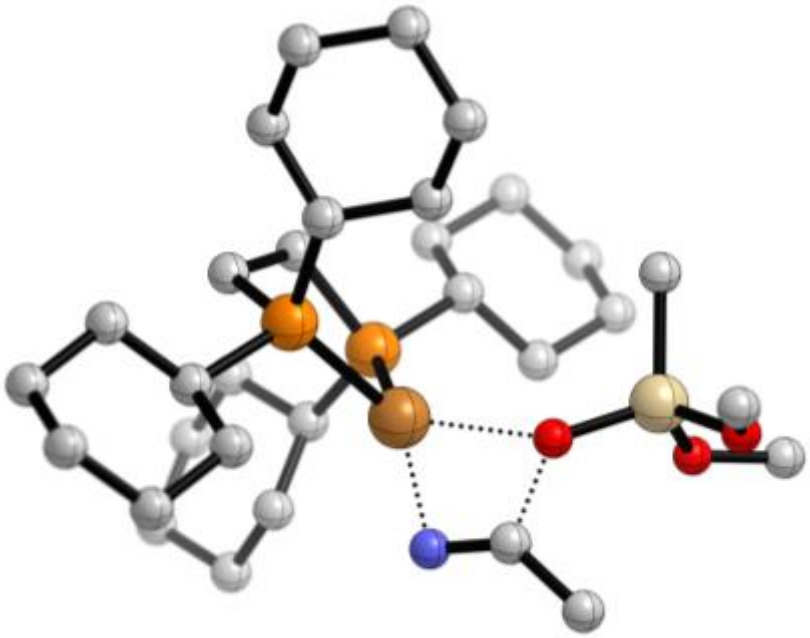
Figure SI-1. Elimination from disilyl imidate intermediate, with 3D rendering of DFT-optimized transition state structure.

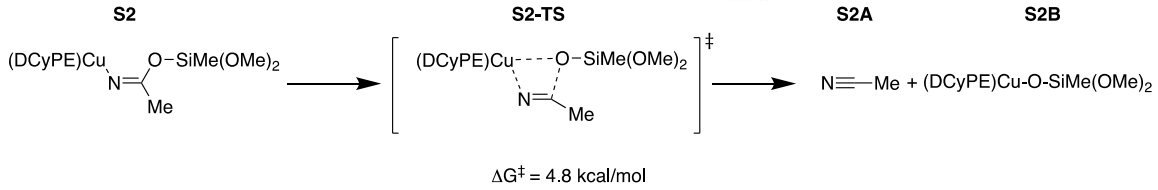


Elimination from Copper Silyl Imidate

We modeled the analogous elimination from a copper-bound intermediate **S2**, which we propose to be on the mechanistic cycle of our reported transformation. Using DCyPE as the supporting ligand, this elimination is predicted to have a very low barrier (4.8 kcal/mol).

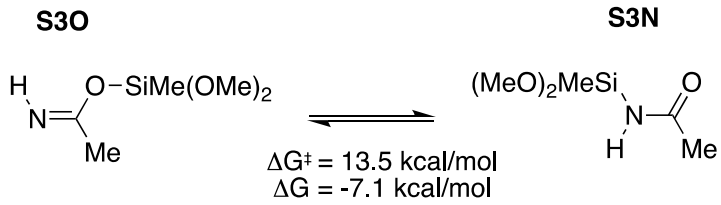
Figure SI-2. Elimination from copper-bound silyl imidiate intermediate, with 3D rendering of DFT-optimized transition state structure.





Interconversion of O-Silyl and N-Silyl Imidate Forms

We note that the *O*-silyl and *N*-silyl imidate forms of **S3** are predicted to equilibrate rapidly at room temperature, which is important since the *N*-silyl form is lower in energy, but our proposed mechanism requires that the silyl group be connected to the oxygen atom during the elimination step. A similar observation has previously been noted in both theoretical and experimental studies (for instance, see refs. 6c, 6d, 6g, 6h, 6p in the manuscript).



Cartesian Coordinates and Calculated Thermodynamic Properties

DCyPECuH
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -1900.375094
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.645239
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -1899.898139
Total Free Energy: -1899.252900

Cu	-0.00120500	-0.00008000	-1.82999500
C	0.70322400	-0.31765300	1.45948800
H	1.25264800	-0.01941000	2.35908900
H	0.61264100	-1.41162100	1.49462800
C	-0.70300400	0.31813800	1.45961800
H	0.00094600	-0.00078100	-3.38408200
H	-1.25232700	0.01980700	2.35925000
H	-0.61246200	1.41210700	1.49480500
P	1.64600700	0.06476400	-0.12420200
P	-1.64591400	-0.06440500	-0.12391600
C	2.99247500	-1.24672300	-0.12392200
C	3.80195700	-1.19308700	-1.43857000
C	3.93578200	-1.30101700	1.09466500
H	2.41013300	-2.18256800	-0.14119000
C	4.78731300	-2.36986400	-1.53892400
H	4.36862200	-0.25062900	-1.48108700
H	3.12072800	-1.18801000	-2.29688700
C	4.91312900	-2.48638900	0.99084000
H	4.51587100	-0.36908500	1.14784500
H	3.36341000	-1.37131700	2.02815100
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H	5.58962600	-2.48736100	1.85543700
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H	6.37229000	-1.55970200	-0.30822400
C	2.52242300	1.71526000	0.17437800
C	1.77477700	2.85640400	-0.55393100
C	2.79714100	2.10878200	1.64063200
H	3.49305900	1.58888800	-0.32952100
C	2.54125200	4.18586000	-0.46124900
H	0.77944500	2.98351900	-0.10076000
C	2.54125200	4.18586000	-0.46124900
H	0.77944500	2.98351900	-0.10076000
H	1.60365800	2.58393700	-1.60160200
C	3.57149400	3.43681800	1.72943100
H	1.84154600	2.22332500	2.17282400
H	3.35267800	1.32125700	2.16195300
C	2.84122200	4.57028000	0.99482500
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H	3.48762800	4.09302100	-1.01467100
H	3.73031400	3.70298500	2.78258500
H	4.56988500	3.30139400	1.28759800
H	3.43568500	5.49199000	1.03249500
H	1.89582500	4.78709800	1.51477500
C	-2.99266200	1.24673000	-0.12378200
C	-3.80238500	1.19251700	-1.43824300
C	-3.93569600	1.30125500	1.09499300
H	-2.41048600	2.18267300	-0.14150100
C	-4.78779700	2.36921500	-1.53883800
H	-4.36903800	0.25003100	-1.48027100
H	-3.12122200	1.18703000	-2.29661200
C	-4.91319900	2.48647800	0.99096400
H	-4.51564800	0.36926000	1.14858200
H	-3.36313800	1.37192800	2.02833300
C	-5.71621200	2.44250600	-0.31742700
H	-5.37589600	2.28190900	-2.46105700
H	-4.21883800	3.30728200	-1.61967200

H	-5.58959300	2.48763000	1.85564000
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H	-1.60225600	-2.58381700	-1.60103200
C	-3.57089800	-3.43681100	1.72950600
H	-1.84134800	-2.22290600	2.17328700
H	-3.35267100	-1.32117400	2.16191900
H	-1.84134800	-2.22290600	2.17328700
H	-3.35267100	-1.32117400	2.16191900
C	-2.84015100	-4.57017900	0.99523400
H	-1.96689300	-4.98009400	-0.95584500
H	-3.48604900	-4.09326800	-1.01451700
H	-3.72998000	-3.70291100	2.78263500
H	-4.56918200	-3.30164300	1.28735400
H	-3.43441400	-5.49202100	1.03282900
H	-1.89485800	-4.78673100	1.51548800

DiSilyl Imidate (S1)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -1327.57299996
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.243935
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -1327.140658
Total Free Energy:

C	1.12780000	-2.50480400	-0.99825800
H	1.82988500	-1.99822200	-1.67157900
H	1.72252300	-2.95595300	-0.19786000
H	0.58757100	-3.27382400	-1.55122800
C	0.14817800	-1.50871300	-0.43132200
N	-1.09203400	-1.54528800	-0.67927400
O	0.69569600	-0.56956900	0.40633700
Si	-2.31221700	-0.43788500	-0.16253700
O	-1.83709900	1.12603000	-0.53208200
O	-2.51596000	-0.62985700	1.47578900
C	-3.90279300	-0.84458300	-1.07088100
H	-4.75980000	-0.24769000	-0.73719800
H	-3.78836200	-0.69355100	-2.15083800
H	-4.14941900	-1.90013900	-0.91157300
C	-2.69932600	2.19155700	-0.88753700
H	-2.08851300	3.00903700	-1.28590000
H	-3.42431100	1.89971600	-1.65911500
H	-3.25315000	2.57421900	-0.01853600
C	-3.36346900	0.16178900	2.28529200
H	-4.39689200	0.18495200	1.90810900
H	-3.37965700	-0.27120400	3.29081700
H	-2.99623400	1.19485500	2.36087600
Si	2.12235500	0.29619400	0.38750900
O	3.36705100	-0.77000100	0.57000100
O	2.35031600	1.01661400	-1.08246600
C	1.97677000	1.50756700	1.79646300
H	1.14139200	2.19778600	1.63575400
H	1.79258300	0.97548000	2.73588500
H	2.89161300	2.09975200	1.91323000
C	4.73077300	-0.48427500	0.28737400
H	5.15018700	0.21856700	1.02016100
H	5.29124300	-1.42185000	0.34957900
H	4.85003500	-0.06252100	-0.71714700
C	1.48302500	1.99893800	-1.64602800
H	1.63628500	2.97487400	-1.16639400
H	1.72972800	2.09318900	-2.70791800
H	0.42981600	1.71262100	-1.54504800

DiSilyl Imidate Elimination TS (S1-TS)

Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -1327.53347287
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.245772
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -1327.32745577
Total Free Energy: -1327.081683

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H	1.61861900	-1.80568100	-2.35312100
H	1.63326100	-2.71984600	-0.83939500
H	0.83206500	-3.41357200	-2.29668100
C	-0.22803600	-1.87957700	-1.34596100
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O	0.19584100	-0.45085400	-0.22170500
Si	-1.65511800	-0.19816400	-0.10668700
O	-1.33207200	1.40226200	-0.56653600
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H	-3.72713900	-0.14151000	-1.52095600
H	-3.89728700	-1.31023400	-0.21971500
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H	-3.01284600	2.16318600	-1.55679600
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C	-2.64089600	-0.71180200	2.42138500
H	-3.31276400	-1.52862700	2.12933800
H	-2.23133600	-0.94158200	3.41088600
H	-3.23333600	0.20954400	2.50122500
Si	1.55518800	0.30130700	0.36295100
O	2.56643300	-0.96362000	0.73515400
O	2.35719500	1.12253100	-0.83755200
C	1.18836500	1.38540600	1.83618100
H	0.58678200	2.25126100	1.54197200
H	0.61321100	0.81756300	2.57324100
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C	3.93152200	-0.78839500	1.08521000
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DCyPECu Si Imidate (S2)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2667.59057318
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.793695
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -2667.01345884
Total Free Energy: -2666.219763

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H	3.89343500	0.31902500	-3.44775200
H	3.72027900	-1.43767200	-3.38543500
H	2.56410500	-0.46927900	-4.34020200
C	2.23772300	-0.35951500	-2.23076200
N	1.00855500	-0.22628300	-2.23442000
O	2.99476100	-0.40041600	-0.96775300
Si	4.57254100	-0.57705100	-0.57984900
O	5.20637500	-1.97862100	-1.22614600
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C	4.69675800	-0.59870900	1.29321100
H	4.22282600	0.30182300	1.69882200
H	4.18026900	-1.46679400	1.71951100
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C	6.06277600	-2.89926400	-0.58380600

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H	6.08204300	-3.82203200	-1.17392800
H	7.09244000	-2.51829400	-0.51442300
C	6.82569200	0.69560800	-1.42278100
H	7.12047800	-0.12325400	-2.09226900
H	7.10986000	1.64552400	-1.88802200
H	7.38977400	0.59733500	-0.48223400
Cu	-0.27051900	-0.02157700	-0.88139300
P	-1.70532900	-1.42907300	0.27390600
P	-1.10088200	1.81589800	0.28105800
C	-2.86258600	-0.24088300	1.15809400
C	-2.87777700	-2.54731300	-0.67957600
C	-0.92746700	-2.51059000	1.61533900
C	-2.11900900	1.02167000	1.64875500
C	0.14457200	2.85394500	1.23307700
C	-2.23665700	3.04775400	-0.59640800
H	-3.39580800	-0.71106400	1.99142200
H	-3.62201500	0.04180000	0.41674200
C	-2.07802500	-3.44124900	-1.65348800
C	-3.88445500	-3.38326000	0.13513900
H	-3.44929600	-1.83177000	-1.29284000
C	0.51708800	-2.04926900	1.91919400
C	-1.72098200	-2.66816300	2.92868200
H	-0.85725400	-3.50104000	1.13940900
H	-2.82554800	1.72003900	2.10950200
H	-1.39970000	0.74240500	2.43008700
C	1.22156800	3.40744700	0.27341800
C	-0.41594100	3.96745500	2.14003900
H	0.63891900	2.10864000	1.87684500
C	-2.70029200	2.48051600	-1.95747100
C	-3.44613300	3.57359900	0.20316600
H	-1.57407000	3.90090900	-0.80939700
C	-3.01221300	-4.25398100	-2.56584700
H	-1.44747500	-4.13695900	-1.07939700
H	-1.39735200	-2.82543000	-2.25231000
C	-4.81646500	-4.19337300	-0.78604900
H	-3.33723000	-4.08078100	0.78466900
H	-4.48145500	-2.73959800	0.79370000
C	1.22143200	-3.01787100	2.88357200
H	0.48918400	-1.04805800	2.37629500
H	1.08897800	-1.94424700	0.99064900
C	-1.01820400	-3.64004800	3.89452700
H	-1.80973100	-1.68737100	3.41824900
H	-2.74211600	-3.01397000	2.73410800
C	2.33694300	4.13591400	1.04228300
H	0.75653800	4.11187900	-0.43290500
H	1.64130400	2.59065100	-0.32418700
C	0.71037500	4.68436900	2.90749800
H	-0.94767300	4.70566100	1.52354000
H	-1.14847000	3.56085000	2.84925000
C	-3.49663800	3.52157300	-2.76126800
H	-3.33350200	1.59643100	-1.78506400
H	-1.83546100	2.13282100	-2.53369400
C	-4.23588200	4.62240500	-0.60148000
H	-4.11698400	2.73543400	0.44127800
H	-3.12754300	4.00203000	1.15992900
C	-4.02163600	-5.07991400	-1.75584500
H	-2.41781300	-4.90749100	-3.21650100
H	-3.55537900	-3.56443100	-3.22891100
H	-5.49798500	-4.80374300	-0.17936900
H	-5.44703300	-3.49912000	-1.36113500
C	0.42675900	-3.20787400	4.18371400
H	2.23214300	-2.65122900	3.10436700
H	1.34457900	-3.99197800	2.38685600
H	-1.59051900	-3.71250100	4.82854900
H	-1.01529100	-4.64705000	3.45146800
C	1.77824600	5.23882100	1.95339200
H	3.06214000	4.55377800	0.33325800
H	2.88619700	3.40428800	1.65304100
H	0.28697000	5.49076700	3.52043000
H	1.17943600	3.97451200	3.60492100

C	-4.68708400	4.07084700	-1.96154000
H	-3.84070000	3.07892700	-3.70450600
H	-2.82780200	4.35190700	-3.03275700
H	-5.10260200	4.96045200	-0.01864000
H	-3.60161100	5.50726900	-0.75930600
H	-4.70538600	-5.61401600	-2.42780400
H	-3.48273100	-5.84872700	-1.18219700
H	0.92050100	-3.94407100	4.83076000
H	0.41418900	-2.25973500	4.74217300
H	2.58858500	5.70984600	2.52434600
H	1.33147700	6.03065000	1.33354400
H	-5.20641100	4.84973000	-2.53415700
H	-5.41704300	3.26376300	-1.79796100

DCyPECu Si Imidate Elimination TS (S2-TS)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -2667.58663421
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.795520
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -2667.00766165
Total Free Energy: -2666.212141

C	0.90693300	-2.67423800	-3.80758600
H	1.98285500	-2.85736800	-3.73563300
H	0.39244100	-3.61722400	-3.60077900
H	0.66337600	-2.34069900	-4.82124900
C	0.48922100	-1.62232400	-2.84218500
N	-0.00805500	-0.52879700	-2.79307300
O	0.82443100	-2.31650100	-1.23366300
Si	2.18793700	-3.05287100	-0.75584100
O	2.36607500	-4.61288700	-1.35041500
O	3.51414700	-2.25472400	-1.38666400
C	2.31480500	-3.11758300	1.12445900
H	2.20283500	-2.11730900	1.55814700
H	1.53242800	-3.75195000	1.55840800
H	3.28232700	-3.52074400	1.44833600
C	1.40778500	-5.62906800	-1.13867900
H	0.41354600	-5.33542900	-1.50434500
H	1.72527300	-6.52614300	-1.68246600
H	1.31668800	-5.89285500	-0.07377600
C	4.82111800	-2.79869100	-1.40936900
H	4.84882000	-3.75828200	-1.94004500
H	5.47892700	-2.09077000	-1.92607700
H	5.21673500	-2.95367200	-0.39402800
Cu	-0.13537900	-0.02139600	-0.87664000
P	-2.08448000	0.11087100	0.37831500
P	0.90779300	1.61412600	0.37784500
C	-1.78344300	1.70361400	1.32798300
C	-3.66981100	0.48100200	-0.56176800
C	-2.54259800	-1.20245600	1.65955000
C	-0.31543000	1.84215900	1.78741900
C	2.52720100	1.32439700	1.29152300
C	1.08990300	3.31054500	-0.44396700
H	-2.45460400	1.81246700	2.18692700
H	-2.03046200	2.51608300	0.63209400
C	-3.96416000	-0.64368000	-1.57935000
C	-4.92279900	0.81109500	0.27389500
H	-3.40122900	1.37881600	-1.14130100
C	-1.35109700	-2.15610000	1.90100200
C	-3.10451100	-0.69710100	3.00437600
H	-3.33194900	-1.78623400	1.16101400
H	-0.17684100	2.79607600	2.30772800
H	-0.07936100	1.05166200	2.51224400
C	3.66711200	0.99209600	0.30312600
C	2.96560100	2.41906500	2.28540600
H	2.31886200	0.40856100	1.86788300
C	0.36124200	3.34263500	-1.80732500
C	0.69066100	4.53574100	0.40444000
H	2.16834900	3.38275600	-0.65278700

C	-5.16999900	-0.29586500	-2.46874000
H	-4.17687700	-1.57945100	-1.04028300
H	-3.07671600	-0.82790000	-2.19528100
C	-6.11949100	1.16569900	-0.62744100
H	-5.19094400	-0.05933400	0.88907800
H	-4.71988200	1.63713400	0.96714600
C	-1.74531400	-3.32616500	2.81710500
H	-0.52888400	-1.59488200	2.37013100
H	-0.96108100	-2.52365000	0.94605400
C	-3.50525000	-1.87049500	3.91737600
H	-2.33741100	-0.09911700	3.51771500
H	-3.96490800	-0.03643200	2.84973200
C	4.95858200	0.60834400	1.04629100
H	3.86958700	1.86927600	-0.32982700
H	3.37194600	0.17701600	-0.36623100
C	4.25237500	2.01793900	3.02925600
H	3.15186800	3.35346500	1.73808900
H	2.16920800	2.63009600	3.00983200
C	0.63392100	4.65673500	-2.55732400
H	-0.72241700	3.23881600	-1.64400500
H	0.65835300	2.48235000	-2.41653300
C	0.96802800	5.85059400	-0.34672500
H	-0.38265200	4.48322900	0.63856100
H	1.21999900	4.54040700	1.36394500
C	-6.41473800	0.04685100	-1.63700100
H	-5.38248200	-1.13133500	-3.14760800
H	-4.90941200	0.56321300	-3.10433600
H	-7.00379300	1.36708100	-0.00888800
H	-5.89870800	2.09679700	-1.17019300
C	-2.33307200	-2.83520400	4.14833500
H	-0.87241800	-3.96619300	2.99869400
H	-2.48877100	-3.95171600	2.30073200
H	-3.87747000	-1.48409900	4.87519000
H	-4.34082500	-2.41656400	3.45505400
C	5.38869000	1.68642200	2.05162700
H	5.75853400	0.42191500	0.31887700
H	4.79516500	-0.34059400	1.57770400
H	4.55408500	2.82522300	3.70934600
H	4.04565800	1.13966000	3.65868900
C	0.26510500	5.88436800	-1.71156400
H	0.08036200	4.66418800	-3.50466500
H	1.70133100	4.70462300	-2.82009000
H	0.65093900	6.70250900	0.26893000
H	2.05302400	5.95862100	-0.49325300
H	-7.24430600	0.33804200	-2.29384300
H	-6.74679300	-0.85061800	-1.09359200
H	-2.65709200	-3.68571500	4.76154800
H	-1.54860700	-2.31786900	4.72090100
H	6.28071300	1.36202100	2.60265600
H	5.67304400	2.59911600	1.50645500
H	0.51869000	6.80847300	-2.24652100
H	-0.82414800	5.90264300	-1.55566700

O-Si Imidate (S3O)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -768.403944076
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.147192
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -768.273058426
Total Free Energy: -768.125866

C	3.23007900	0.61024000	-0.28190800
H	3.38604200	1.31823200	0.53933100
H	4.04569900	-0.11696900	-0.28943200
H	3.25329900	1.18669100	-1.21324900
C	1.88753000	-0.06251600	-0.13175100
Si	-0.78765300	0.52308200	-0.09952300
O	-1.28585600	-0.07658600	1.34973900
O	-1.21723900	-0.43747900	-1.36052300

C	-1.55727200	2.19108600	-0.37488400
H	-2.64573800	2.13015600	-0.27250600
H	-1.18625500	2.91917900	0.35395800
H	-1.33175400	2.56483500	-1.37909400
C	-0.56259500	-0.78092200	2.34919500
H	-1.26896400	-1.05806800	3.13794000
H	-0.09150600	-1.68143000	1.94367500
H	0.21928300	-0.14744900	2.78738700
C	-1.36214500	-1.85397800	-1.37060800
H	-1.74366800	-2.13992100	-2.35569400
H	-0.40000900	-2.34163200	-1.19010700
H	-2.07925800	-2.17955500	-0.60671800
O	0.88663300	0.84244900	-0.08275200
N	1.64052300	-1.31095600	-0.04981100
H	2.50442000	-1.85106100	-0.10546000

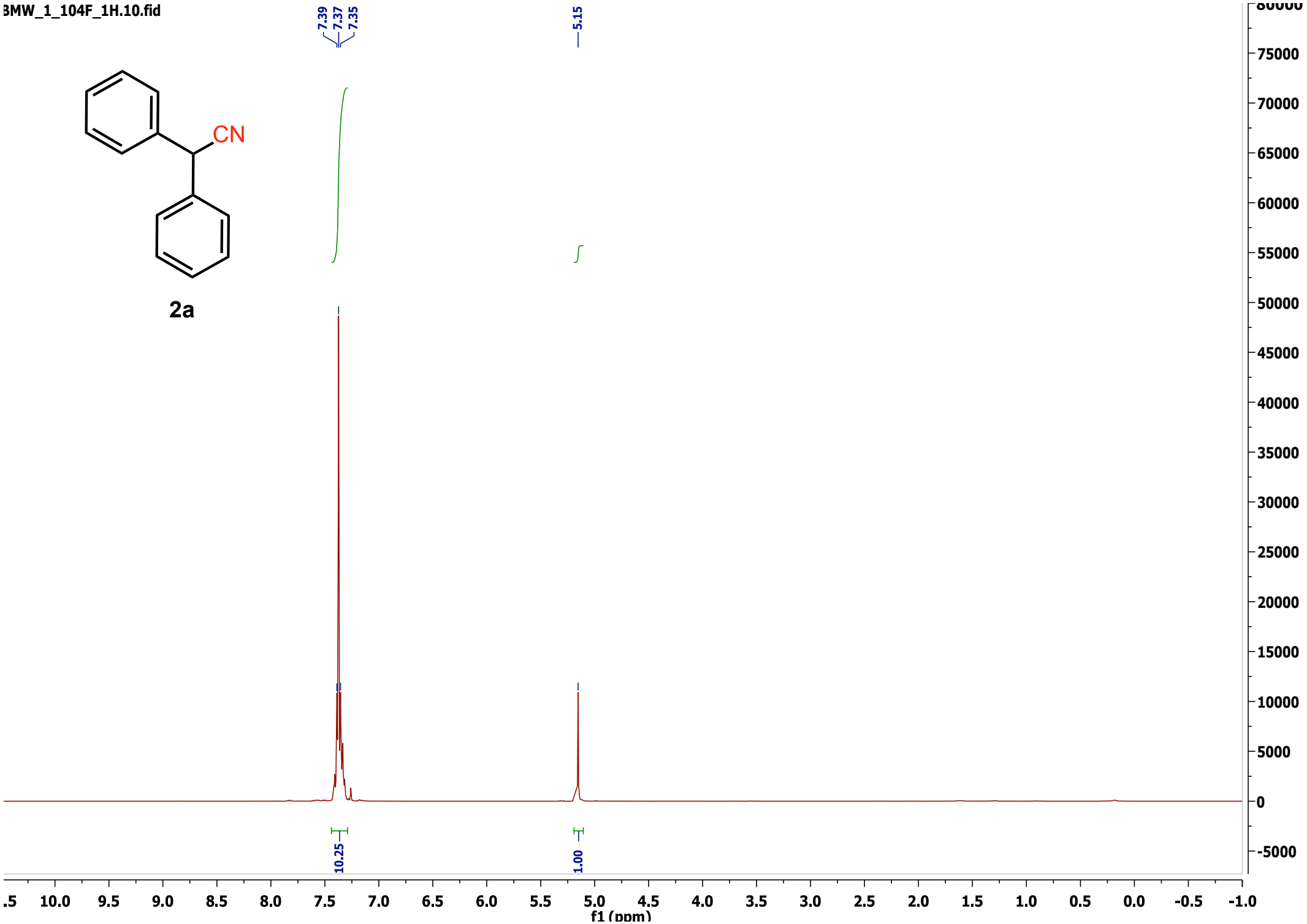
N-Si Imidate (S3N)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 0
Single-Point Energy (B3LYP/SDD-6-31G(d)): -768.399779636
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.146040
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -768.283314289
Total Free Energy: -768.137274

C	3.30942900	0.55973200	-0.30524700
H	3.51007300	1.34770800	0.43011600
H	4.03133600	-0.24785600	-0.17779100
H	3.43533800	0.99608400	-1.30363000
C	1.90256900	-0.00002300	-0.14670100
O	1.68724100	-1.20309300	-0.03458700
Si	-0.85162500	0.50210300	-0.09530700
O	-1.26280600	-0.11929800	1.37605800
O	-1.26711800	-0.50780500	-1.32561100
C	-1.76794300	2.10366300	-0.36466300
H	-2.84089300	1.94737700	-0.21073500
H	-1.44288900	2.88050900	0.33711400
H	-1.62946100	2.47639000	-1.38556000
C	-0.44361100	-0.78692000	2.32658500
H	-1.07400400	-1.04951700	3.18168800
H	0.00210600	-1.69423300	1.90764800
H	0.36658900	-0.13401500	2.67519800
C	-1.22331700	-1.93181600	-1.33636400
H	-1.64888200	-2.26785400	-2.28689500
H	-0.19412500	-2.29049000	-1.24565300
H	-1.82186600	-2.34741300	-0.51612600
H	1.14795800	1.89095200	-0.25504700
N	0.88002500	0.91952500	-0.14065300

Imidate Si-Migration TS (S3-TS)
Charge: 0
Multiplicity: 1
Imaginary Frequencies: 1
Single-Point Energy (B3LYP/SDD-6-31G(d)): -768.380623074
Vibrational Energy (B3LYP/SDD-6-31G(d)): 0.147138
Single-Point Energy (M06/SDD-6-311G+(2d,p)/SMD(THF)): -768.251544168
Total Free Energy: -768.104406

C	-3.18480600	-0.61181200	-0.37323800
H	-3.93045000	0.17580100	-0.50220200
H	-3.26477700	-1.32585000	-1.19955000
H	-3.39077700	-1.16050000	0.55148100
C	-1.79139700	-0.06143100	-0.32731600
O	-0.78317600	-0.87239100	-0.16490400
Si	0.59421700	0.44542100	-0.15109400
O	1.65350400	-0.58891600	-0.93015200
O	0.81619100	0.56949400	1.48990800
C	1.27984100	2.04277700	-0.86248000
H	2.36850500	2.07617600	-0.75289000
H	1.04742100	2.12384300	-1.93042200

H	0.84179300	2.90604000	-0.35119100
C	1.76932900	-1.99502500	-0.82304000
H	2.40794400	-2.34768100	-1.64093500
H	2.24254800	-2.28170300	0.12681000
H	0.79617000	-2.49276000	-0.89379400
C	0.31260300	-0.27189900	2.50879100
H	0.84984200	-0.03859800	3.43424300
H	-0.75862800	-0.09538400	2.67975400
H	0.45233700	-1.33587700	2.28123300
H	-2.05123300	1.92590300	-0.55035100
N	-1.39076000	1.16479100	-0.43314200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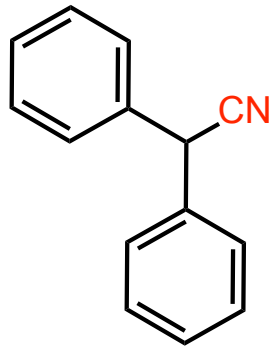

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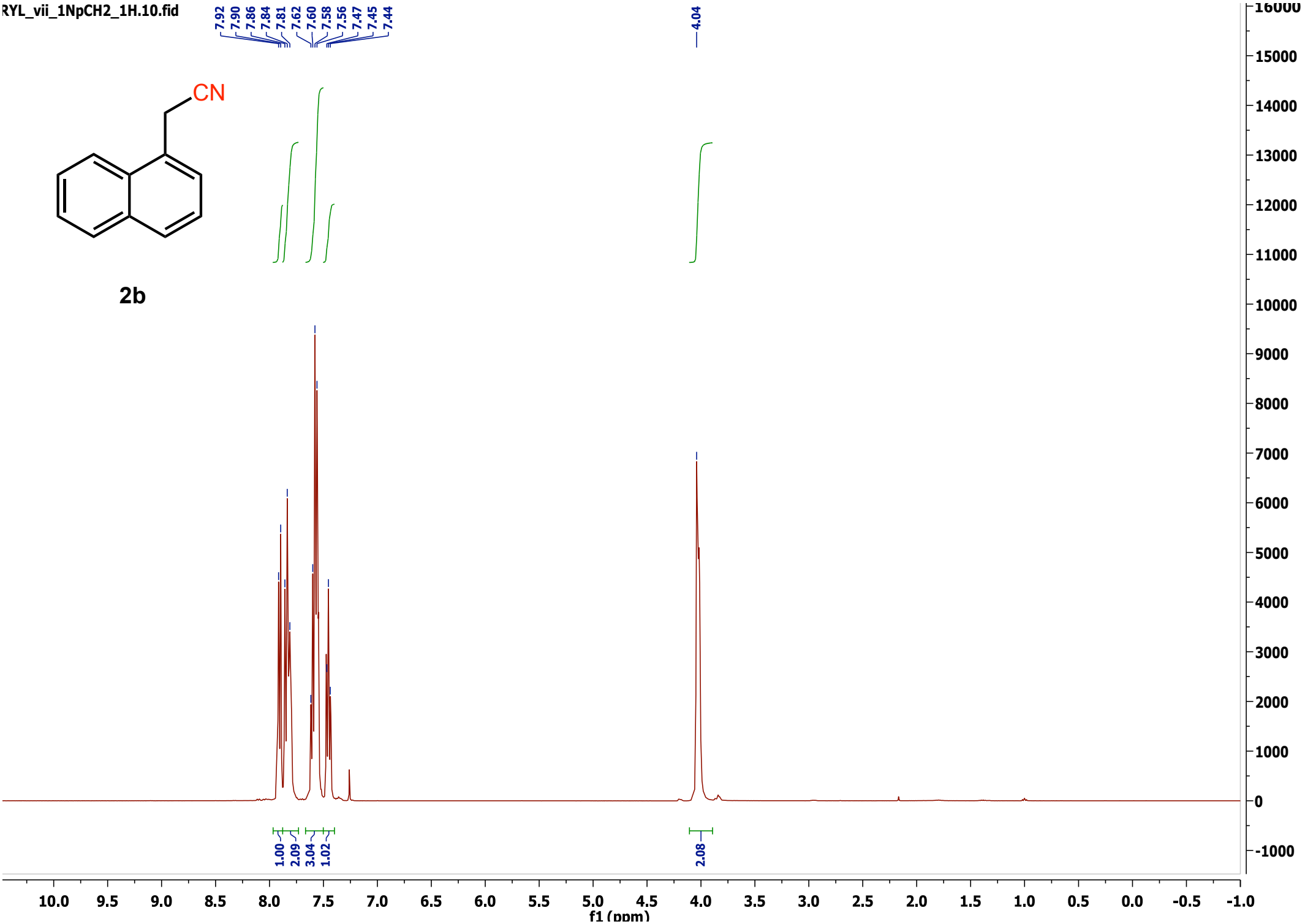
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CN
2b
1.00
2.09
3.04
1.02
2.08
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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0.5
0.0
-0.5
-1.0
f1 (ppm)

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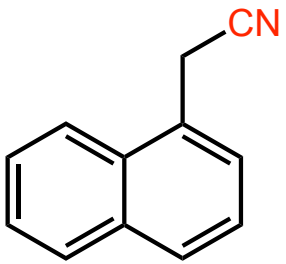

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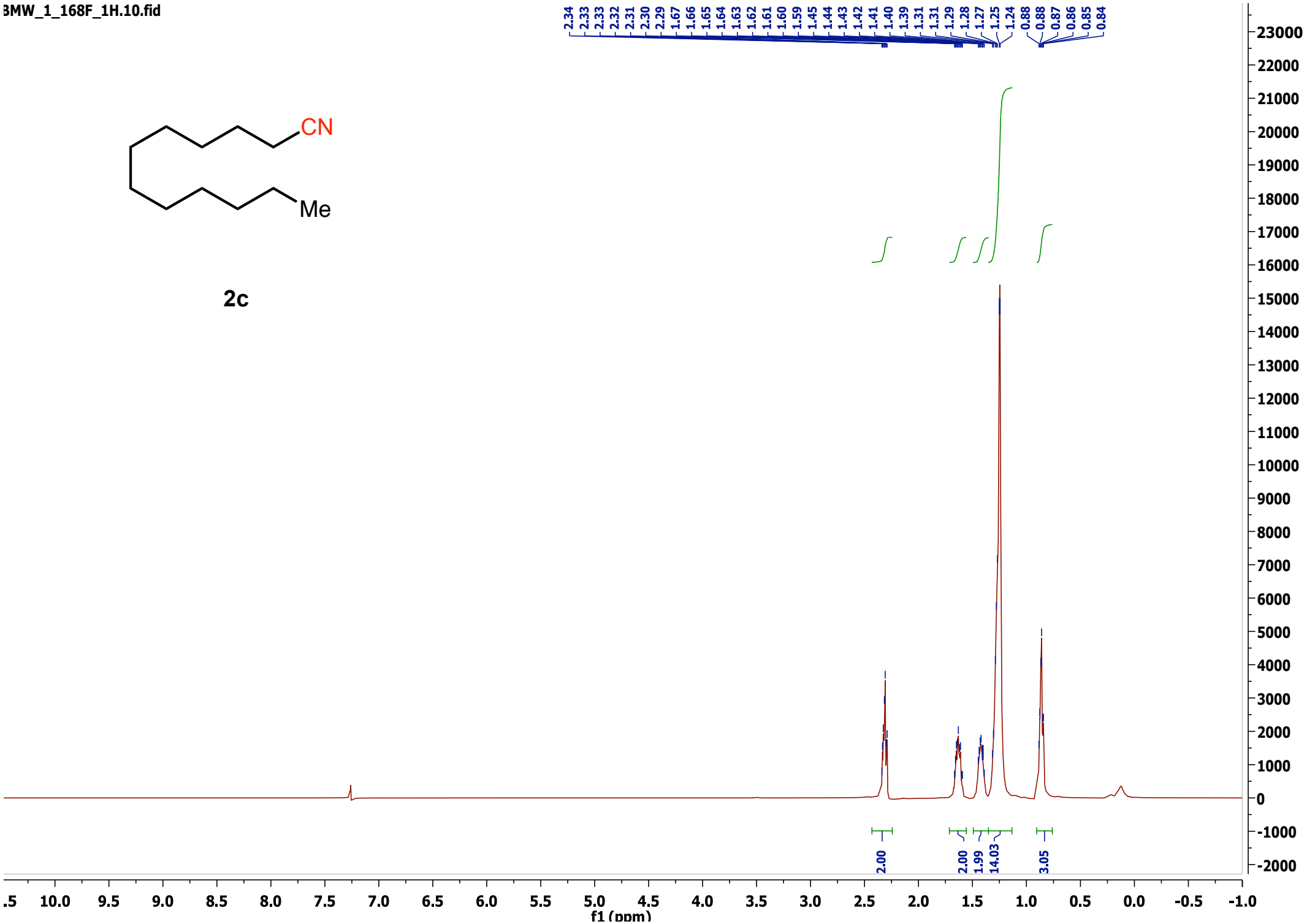
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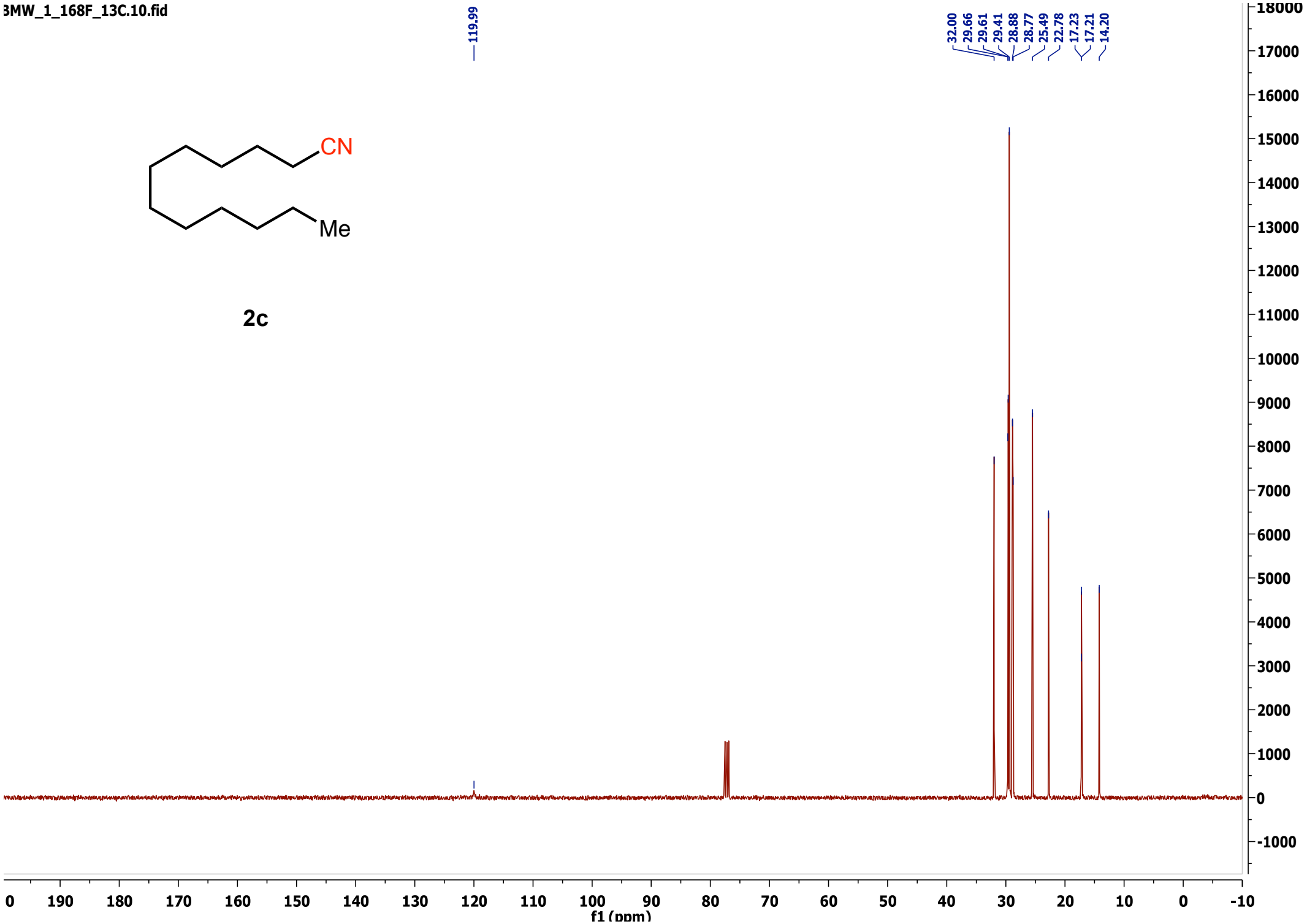
CN
Me
2c
2.00 2.00 1.99 14.03 3.05
f1 (ppm)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CN
Me
2c
f1 (ppm)

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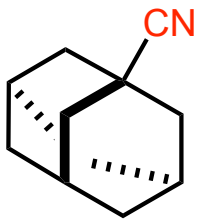
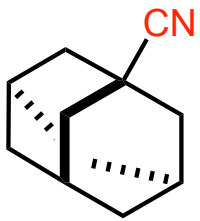


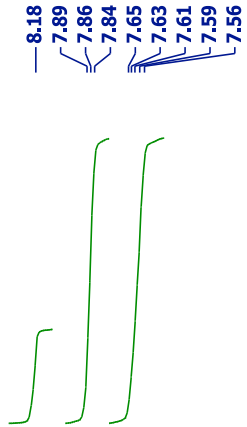
2d

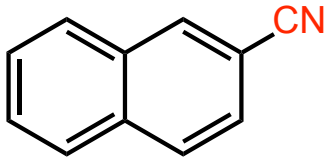
BMW_1_231_13C.10.fid



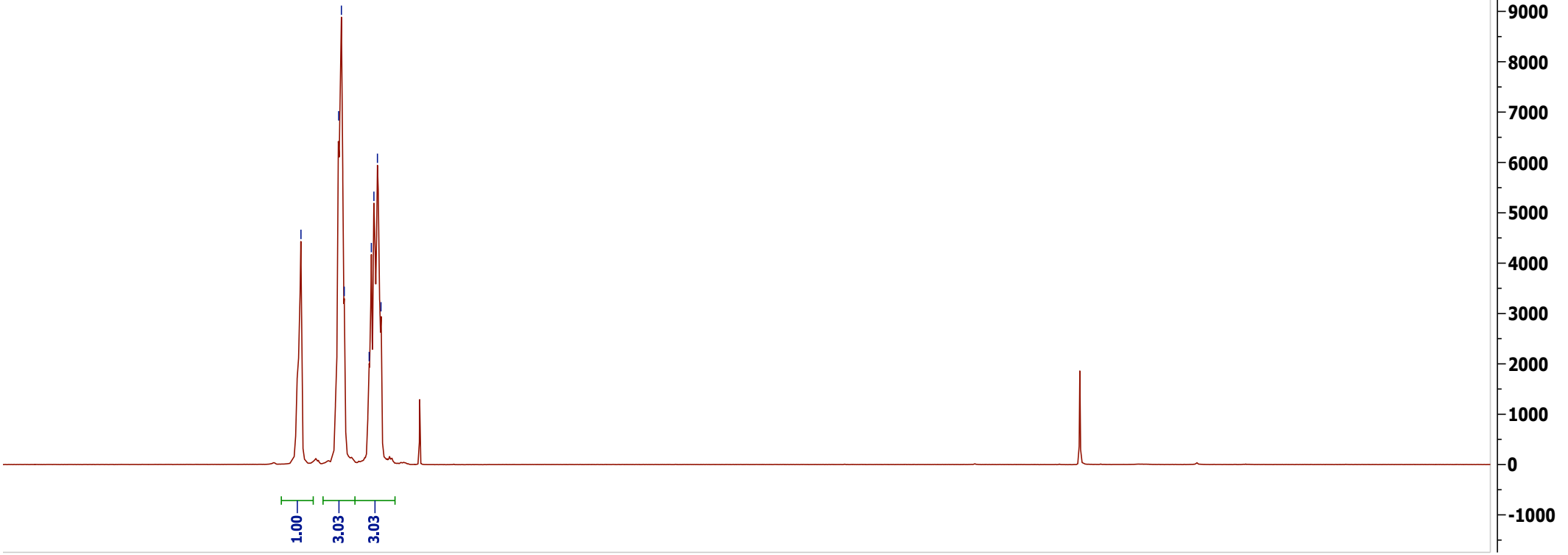
2d

RYL_vii_2Np_2_1H.10.fid



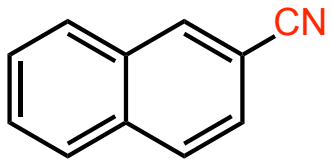


2e



RYL_vii_2Np_2_13C.10.fid

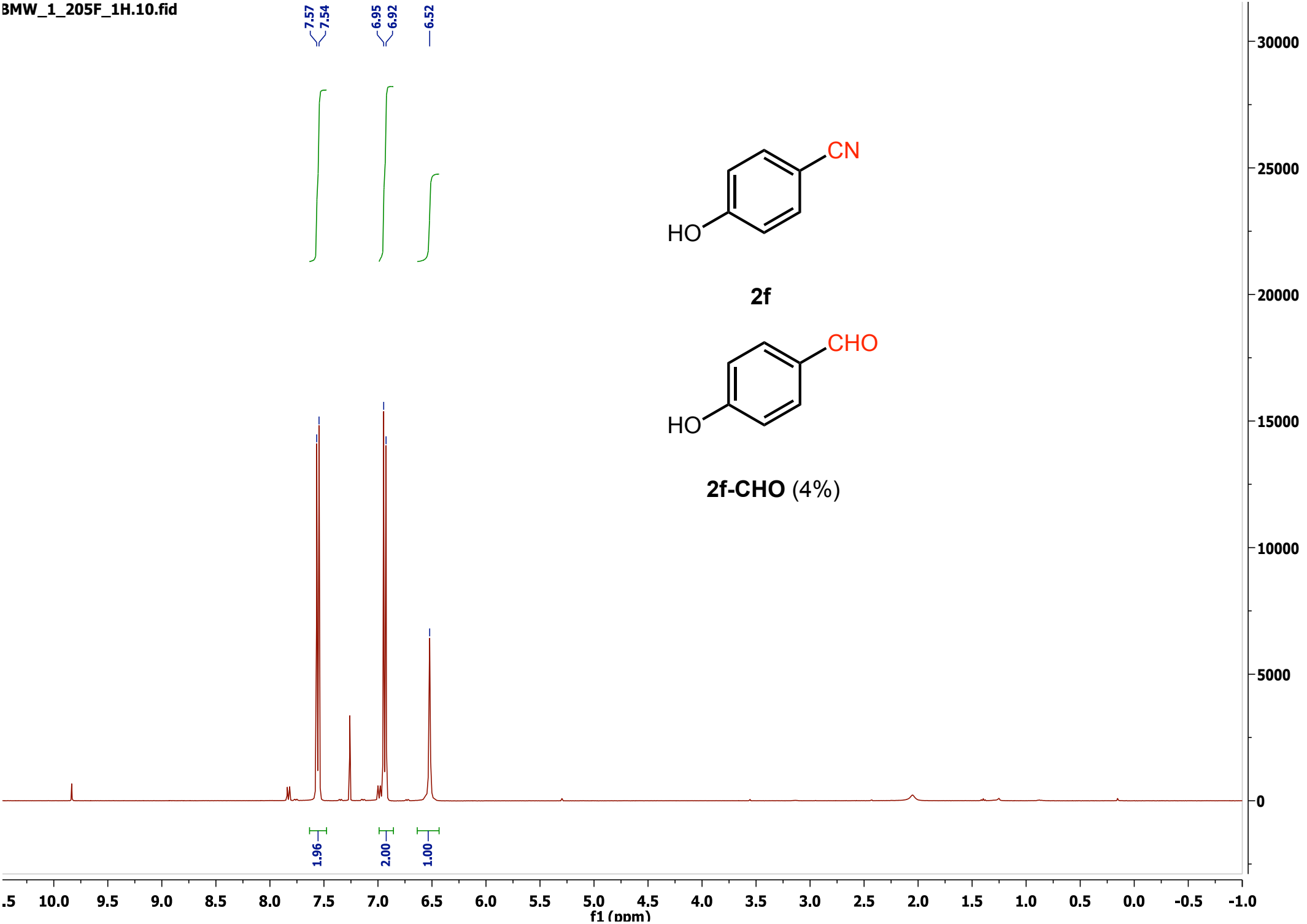
134.66
134.16
132.25
129.23
129.09
128.44
128.09
127.71
126.34
119.31
109.38

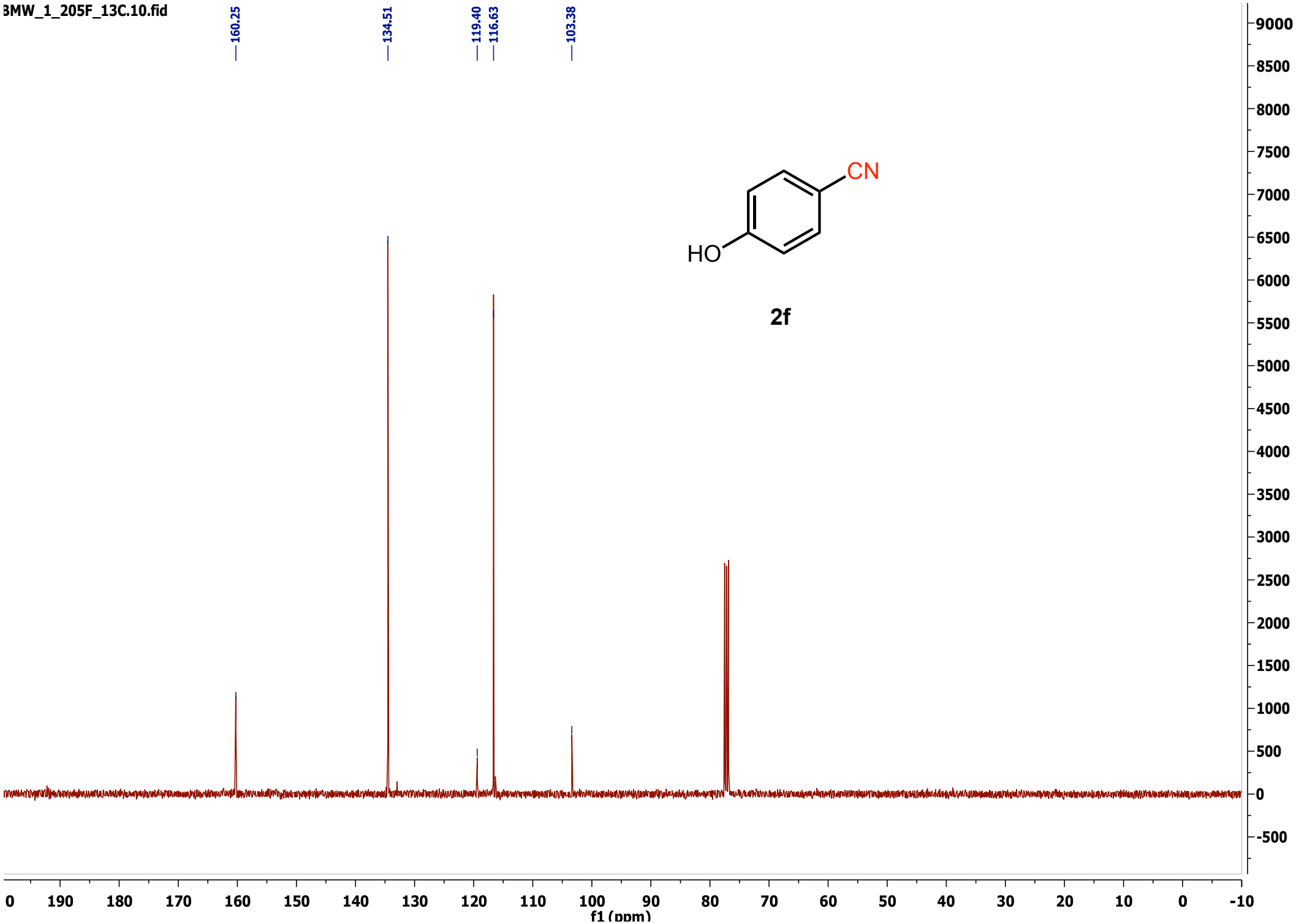


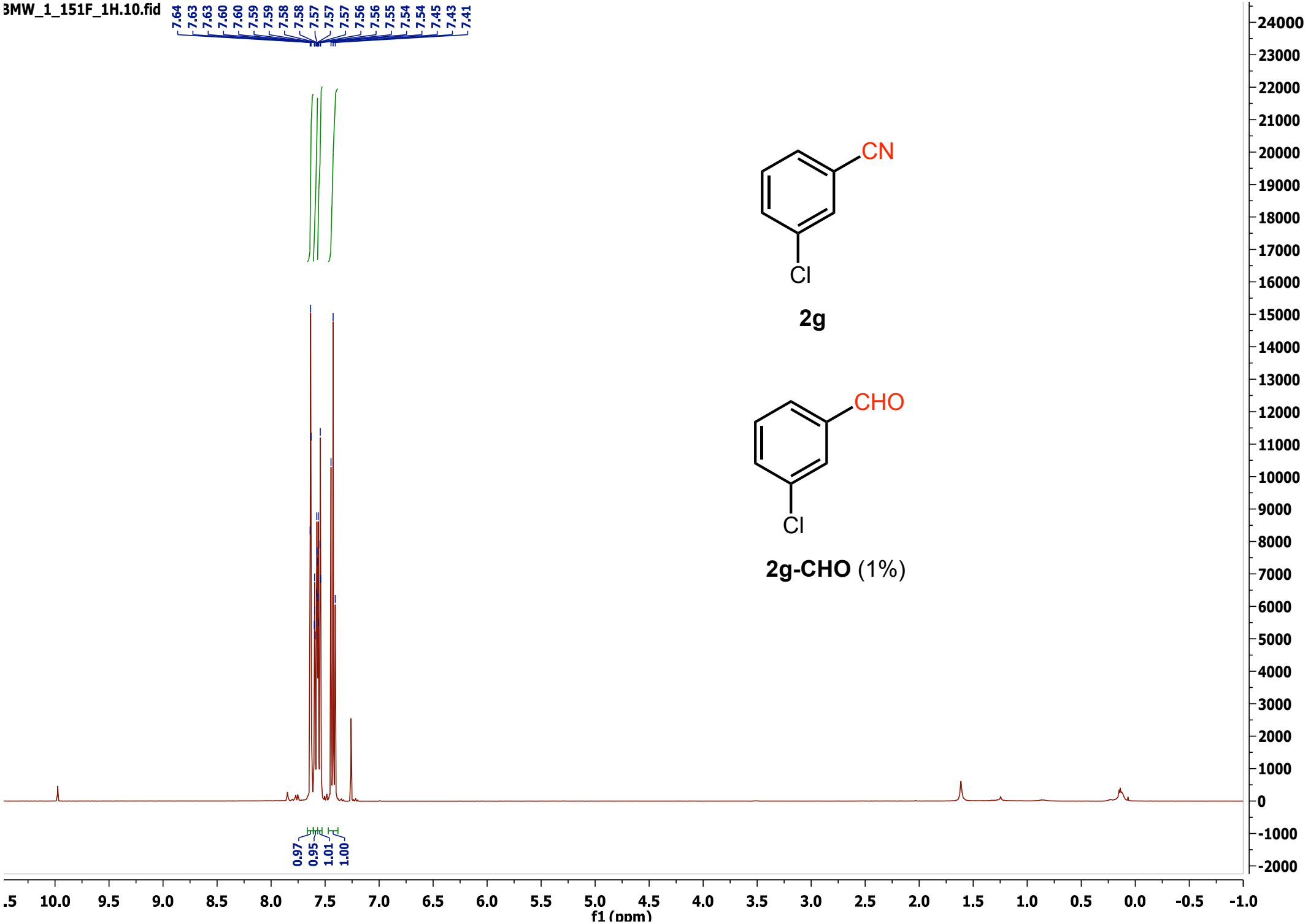
2e

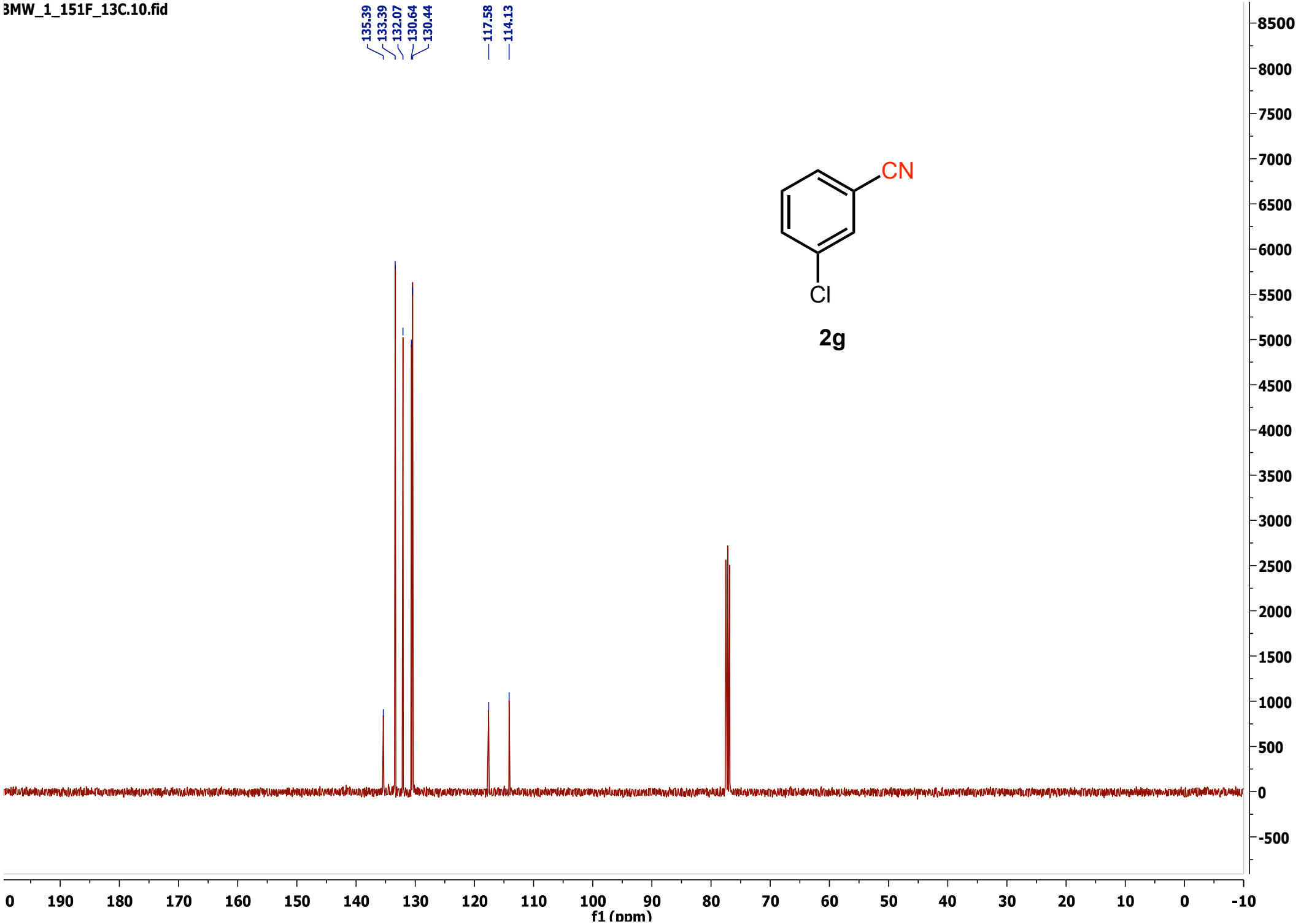
f1 (ppm)

BMW_1_205F_1H.10.fid

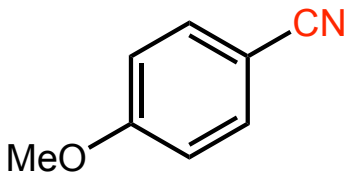



BMW_1_205F_13C.10.fid
160.25
134.51
119.40
116.63
103.38
CN
HO
2f
f1 (ppm)

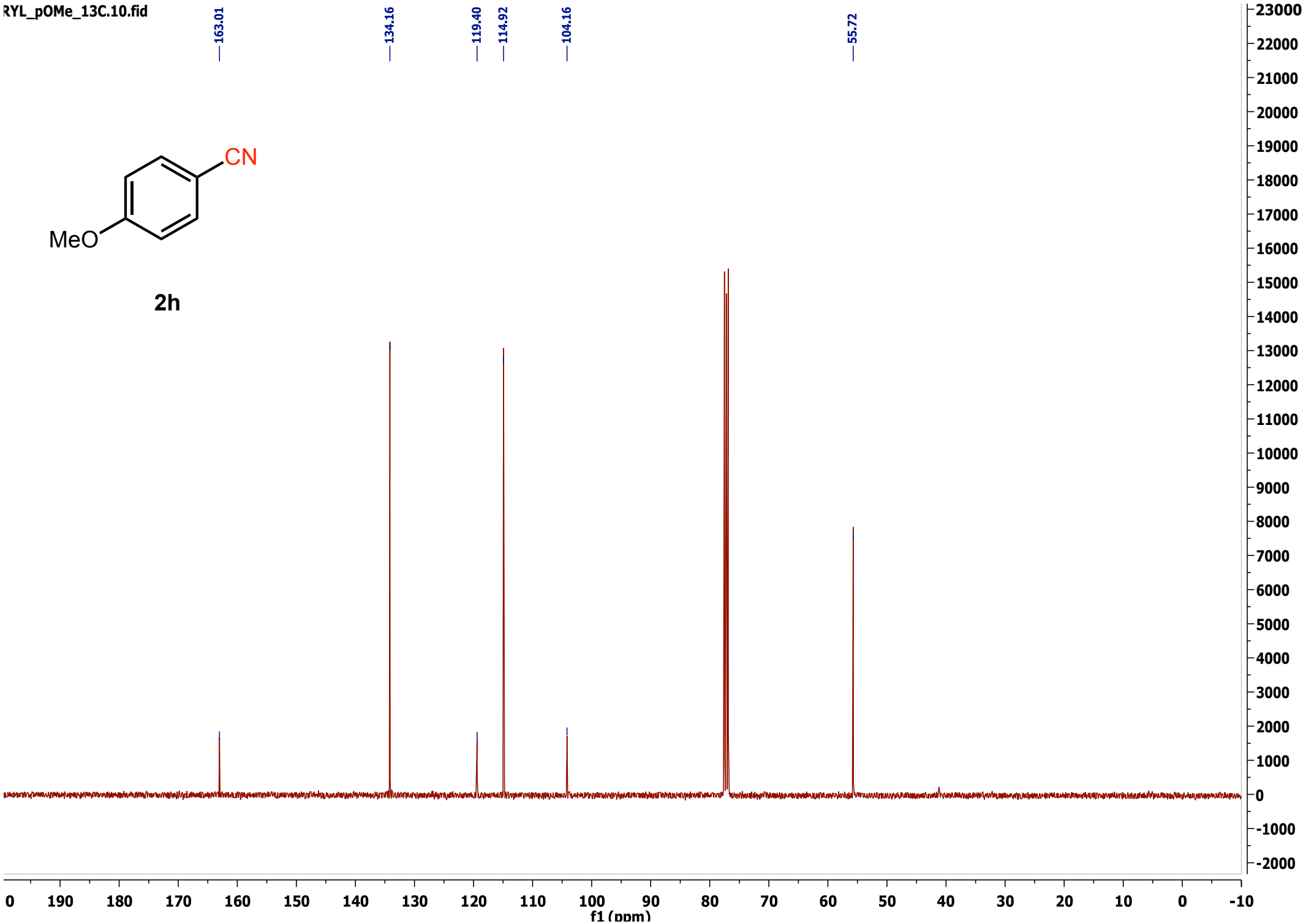

BMW_1_151F_1H.10.fid
7.64 7.63 7.63 7.60 7.60 7.59 7.59 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.55 7.54 7.54 7.45 7.43 7.41
CN
Cl
2g
CHO
Cl
2g-CHO (1%)
0.97 0.95 1.01 1.00
f1 (ppm)

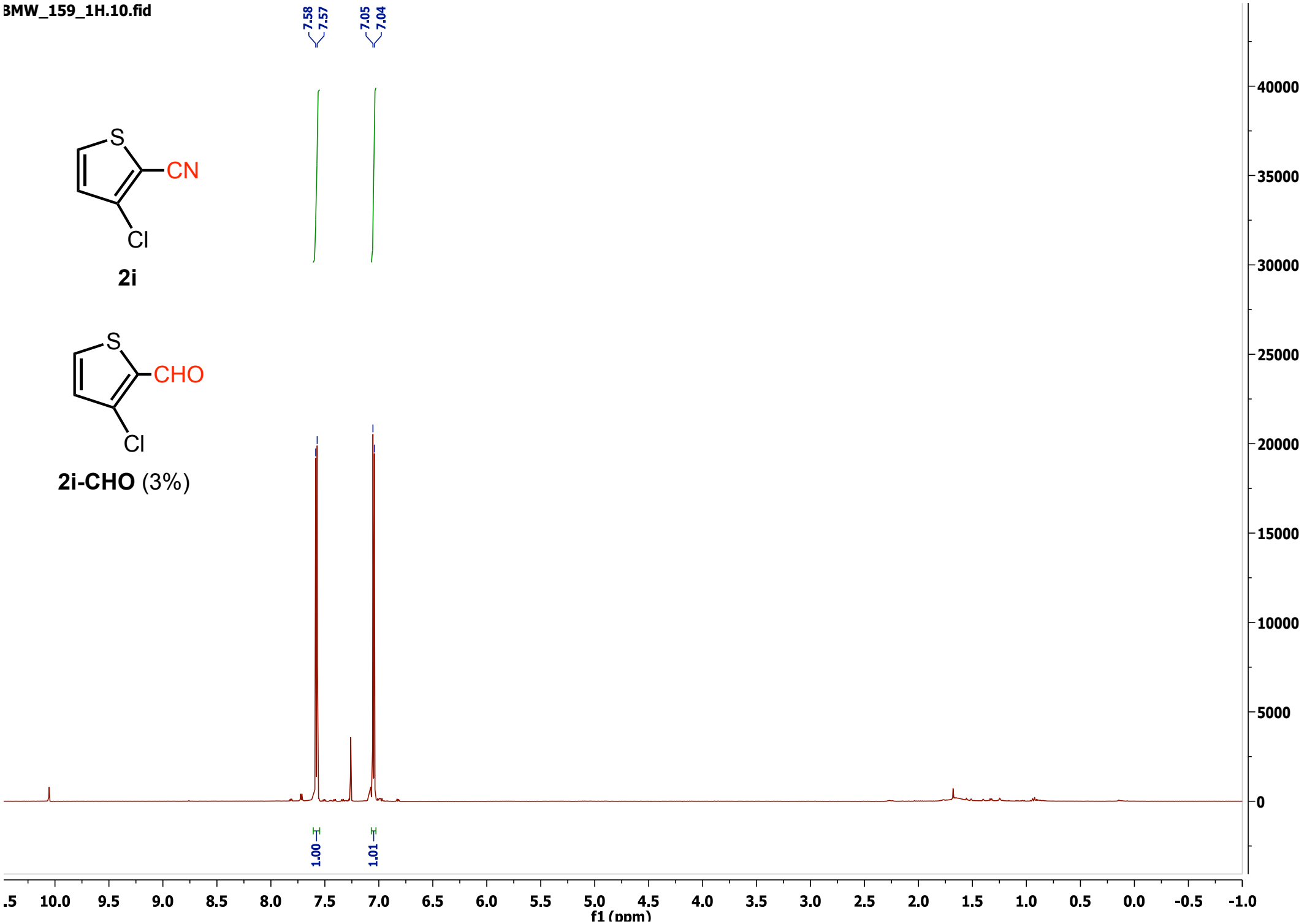

BMW_1_151F_13C.10.fid
135.39
133.39
132.07
130.64
130.44
117.58
114.13
CN
Cl
2g
f1 (ppm)

RYL_pOMe_1H.10.fid

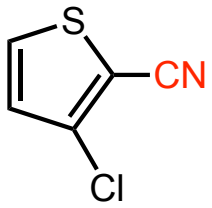


2h


RYL_pOMe_13C.10.fid
163.01
134.16
119.40
114.92
104.16
55.72
CN
MeO
2h
f1 (ppm)

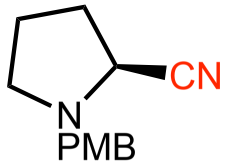

BMW_159_1H.10.fid
7.58
7.57
7.05
7.04
S
CN
Cl
2i
S
CHO
Cl
2i-CHO (3%)
1.00
1.01
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

BMW_159_13C.10.fid



2i

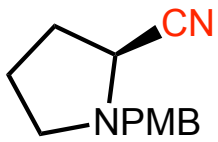
BMW_177_1H.10.fid



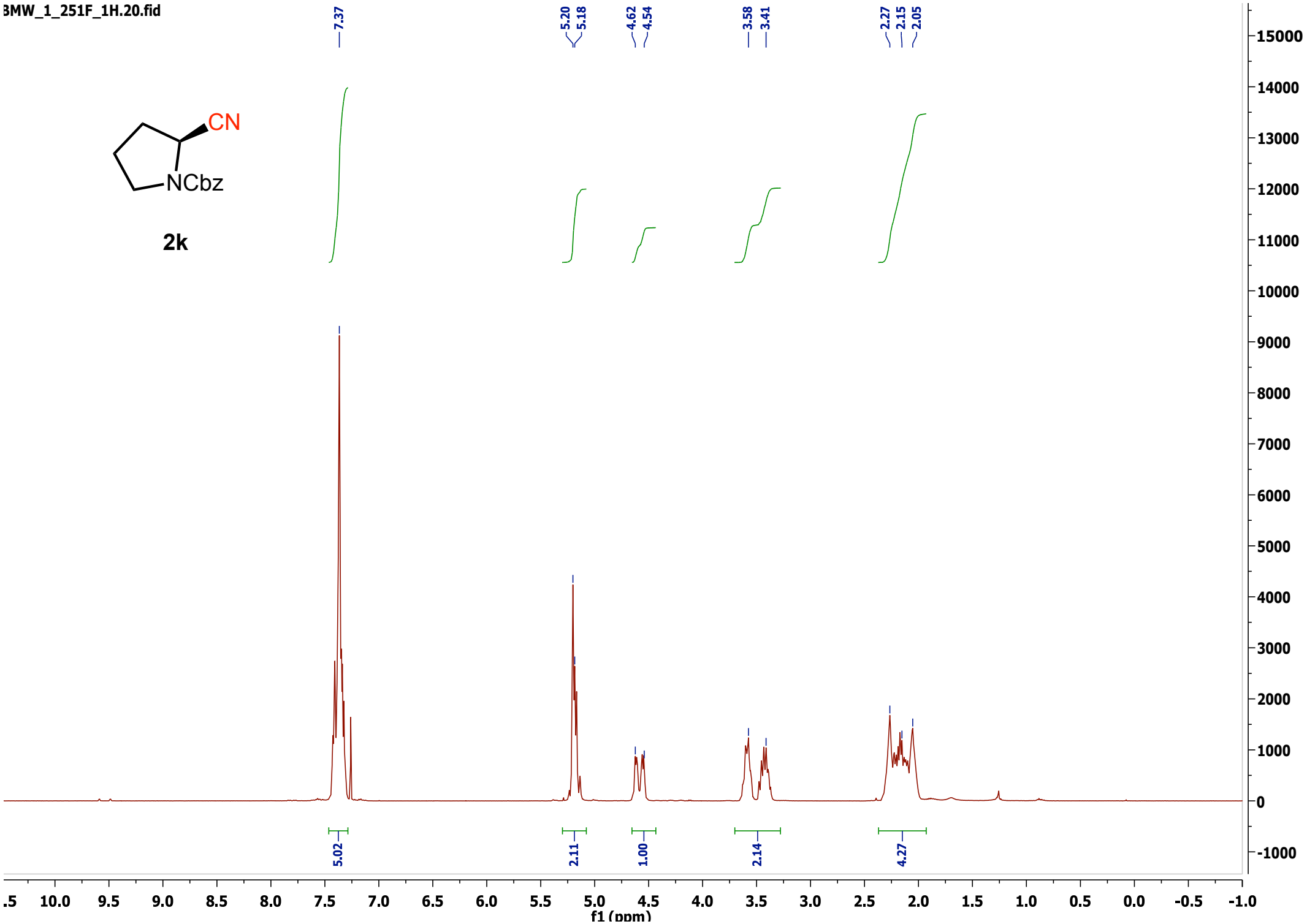
2j

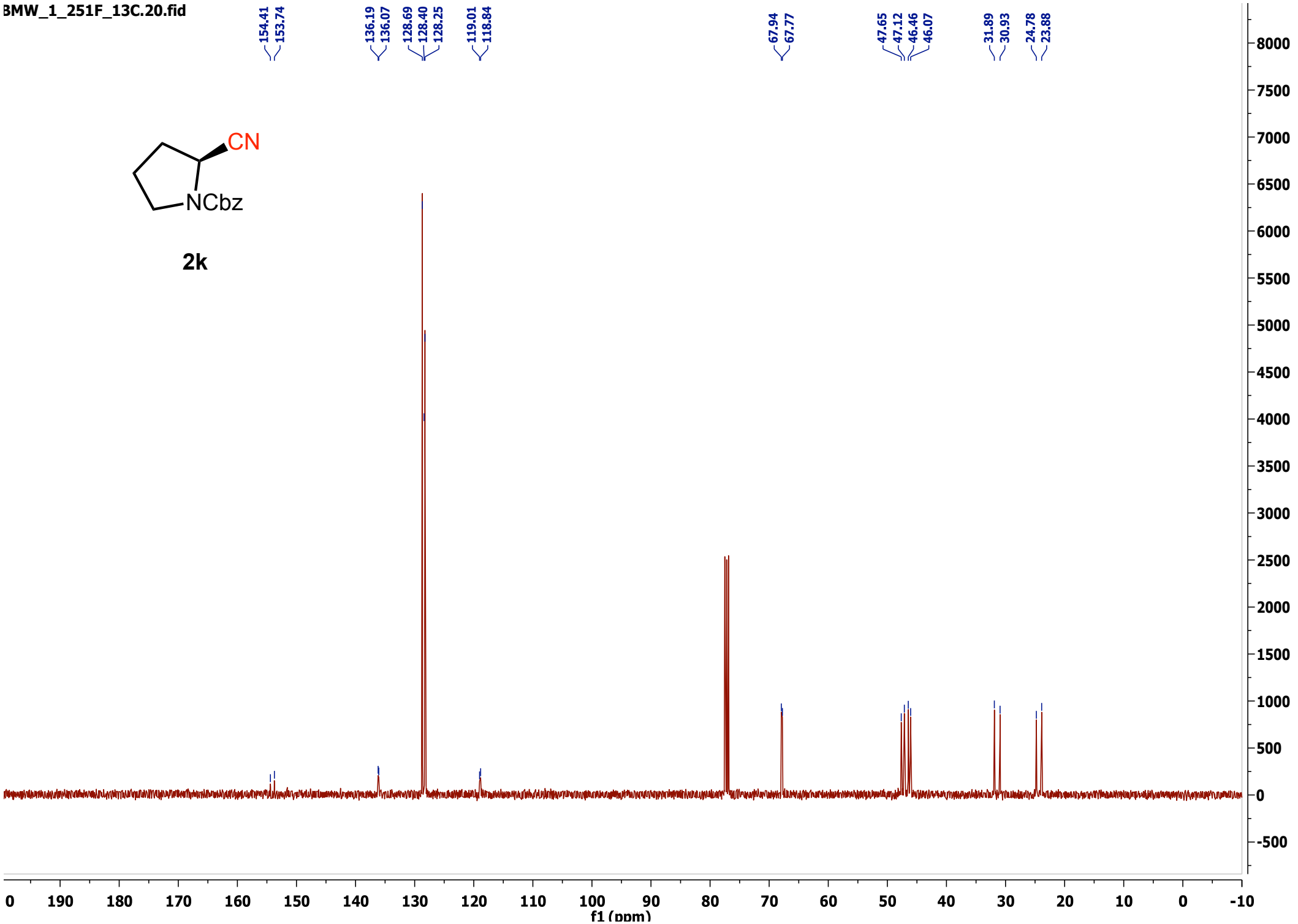
f1 (ppm)

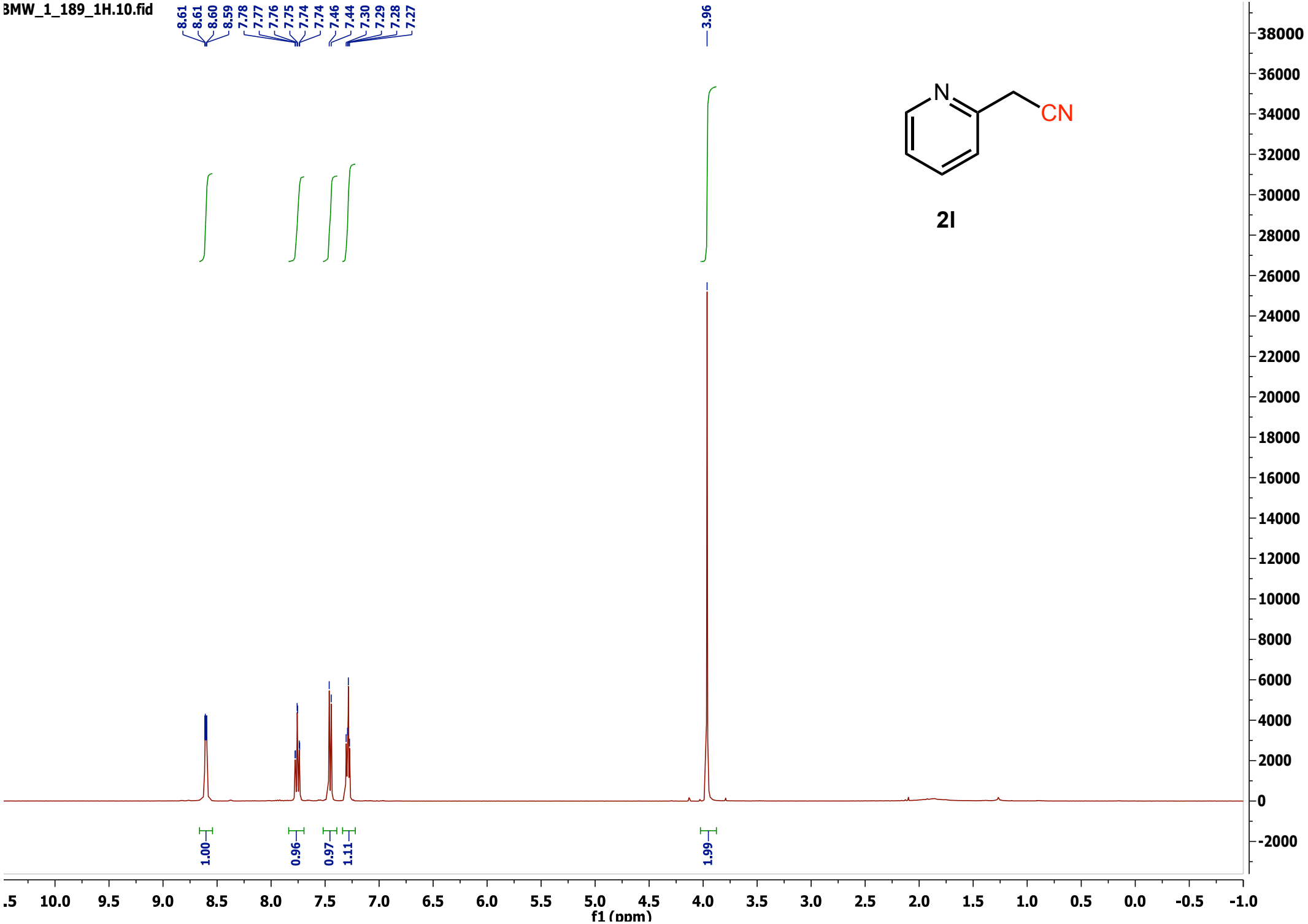
BMW_177_13C.10.fid

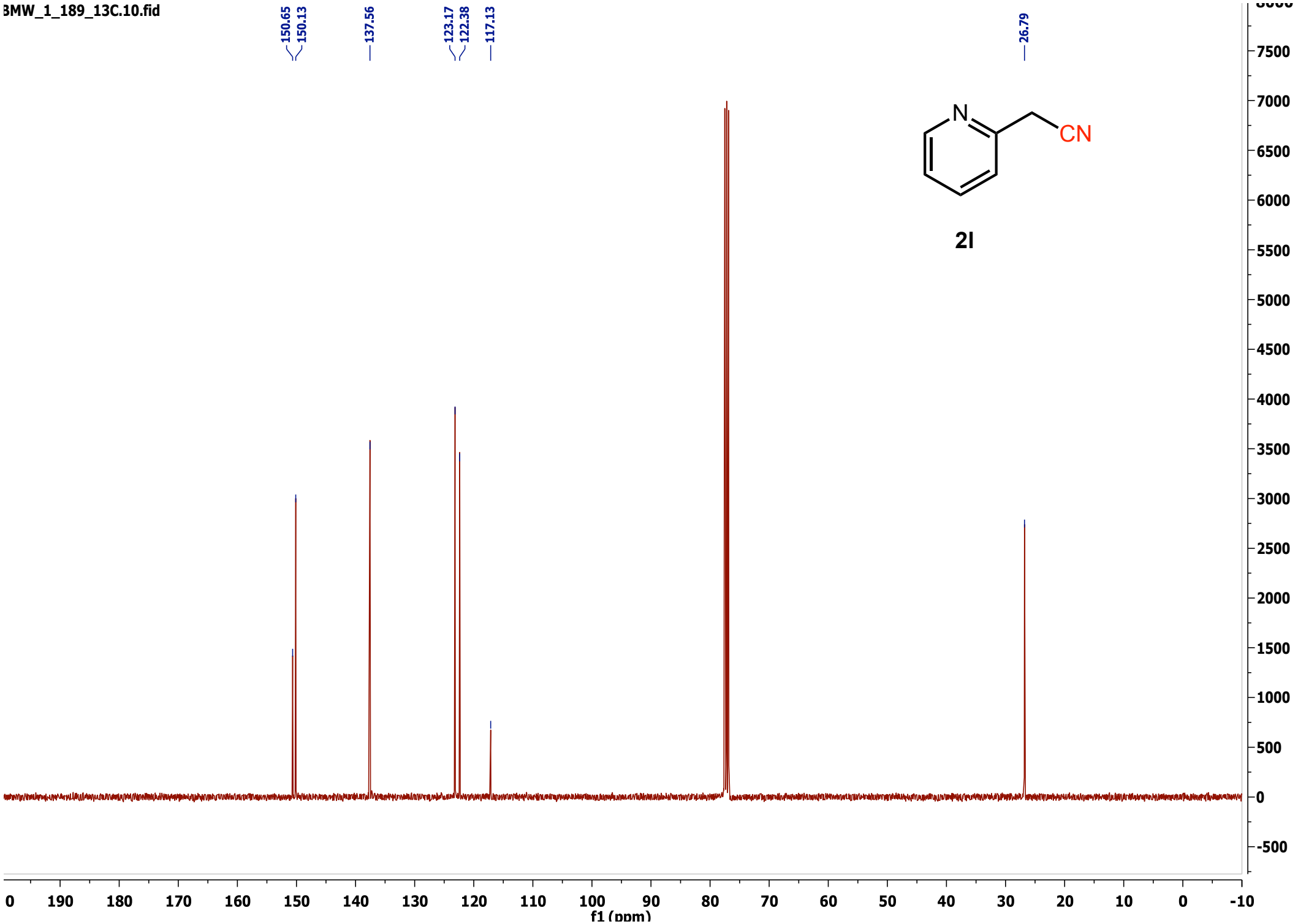


2j

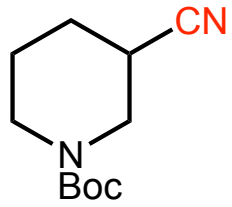

BMW_1_251F_1H.20.fid
7.37
5.20
5.18
4.62
4.54
3.58
3.41
2.27
2.15
2.05
CN
NCbz
2k
5.02
2.11
1.00
2.14
4.27
f1 (ppm)


BMW_1_251F_13C.20.fid
154.41
153.74
136.19
136.07
128.69
128.40
128.25
119.01
118.84
67.94
67.77
47.65
47.12
46.46
46.07
31.89
30.93
24.78
23.88
CN
NCbz
2k
f1 (ppm)

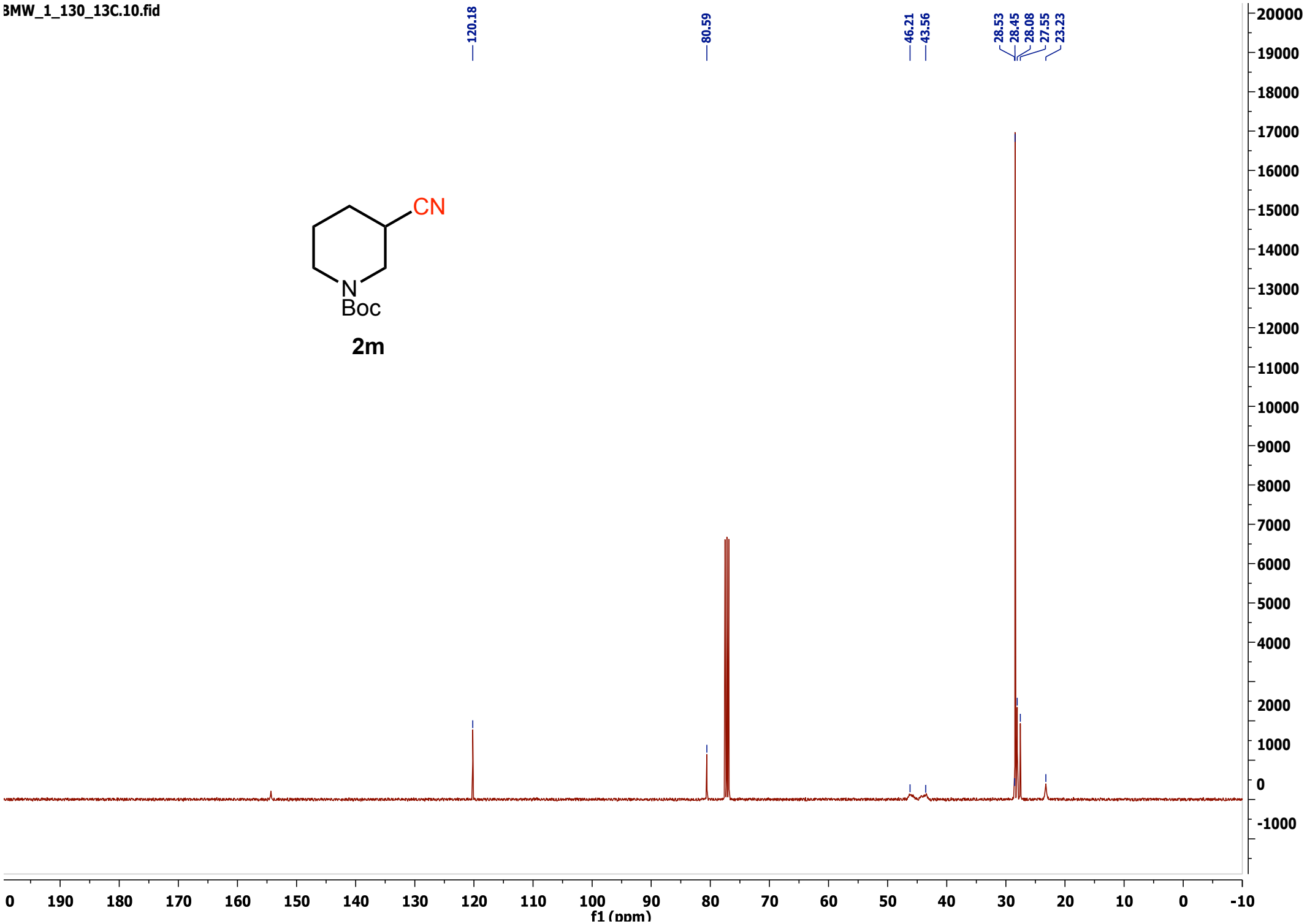

BMW_1_189_1H.10.fid
8.61
8.61
8.60
8.59
7.78
7.77
7.76
7.75
7.74
7.74
7.46
7.44
7.30
7.29
7.28
7.27
3.96
N
CN
2l
1.00
0.96
0.97
1.11
1.99
f1 (ppm)

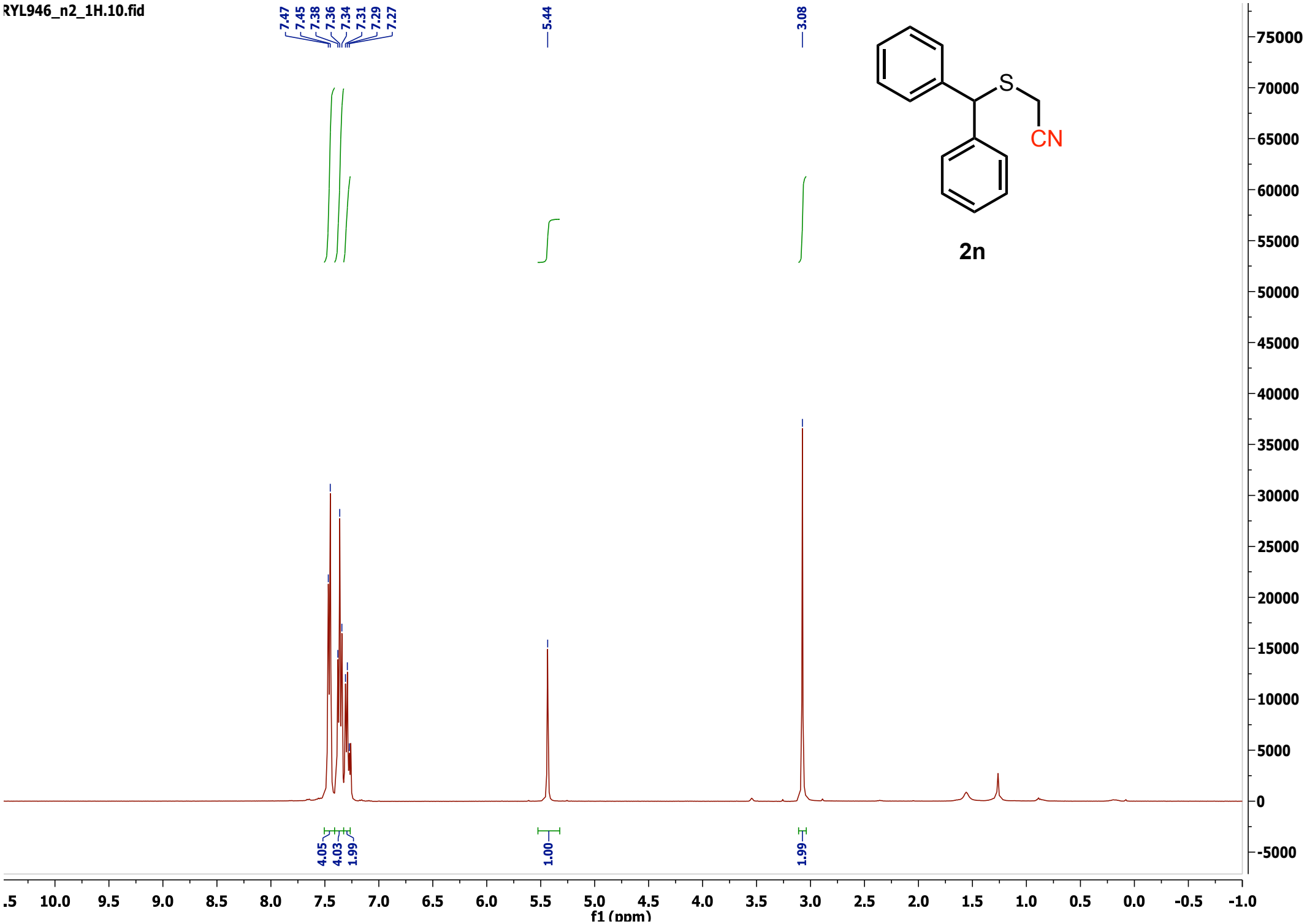

BMW_1_189_13C.10.fid
150.65
150.13
137.56
123.17
122.38
117.13
26.79
N
CN
2l
f1 (ppm)

BMW_1_130_1H.10.fid

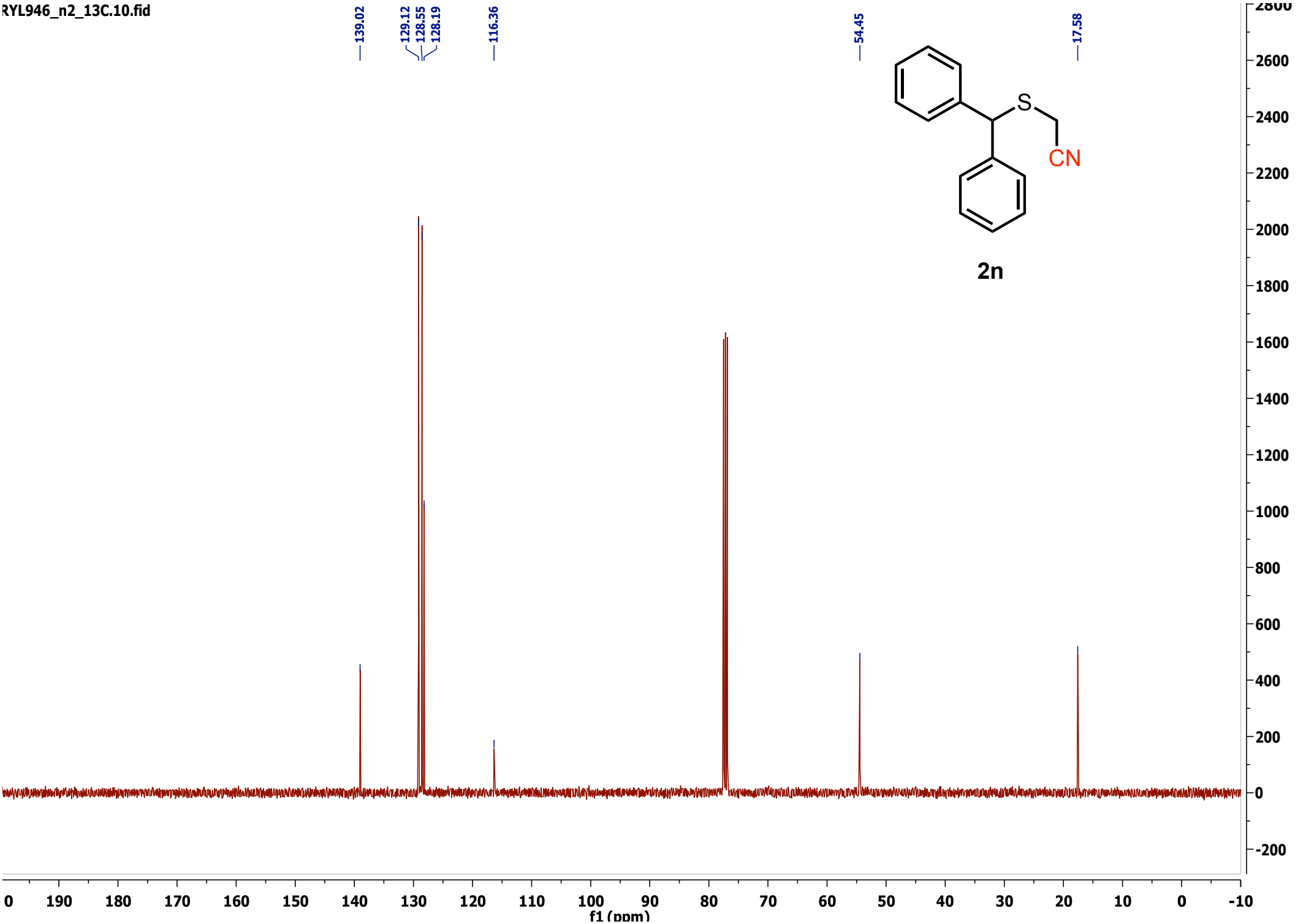


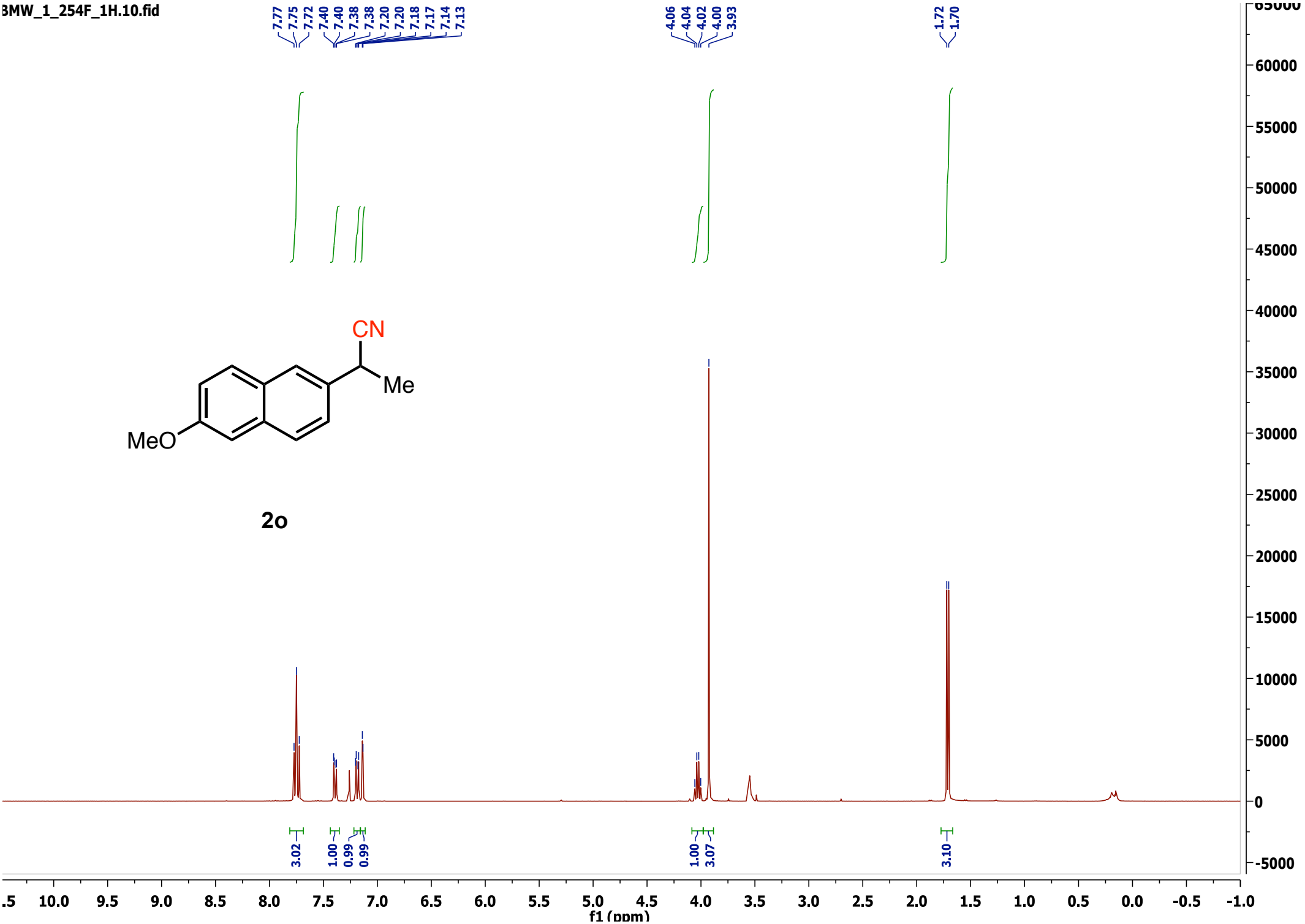
2m

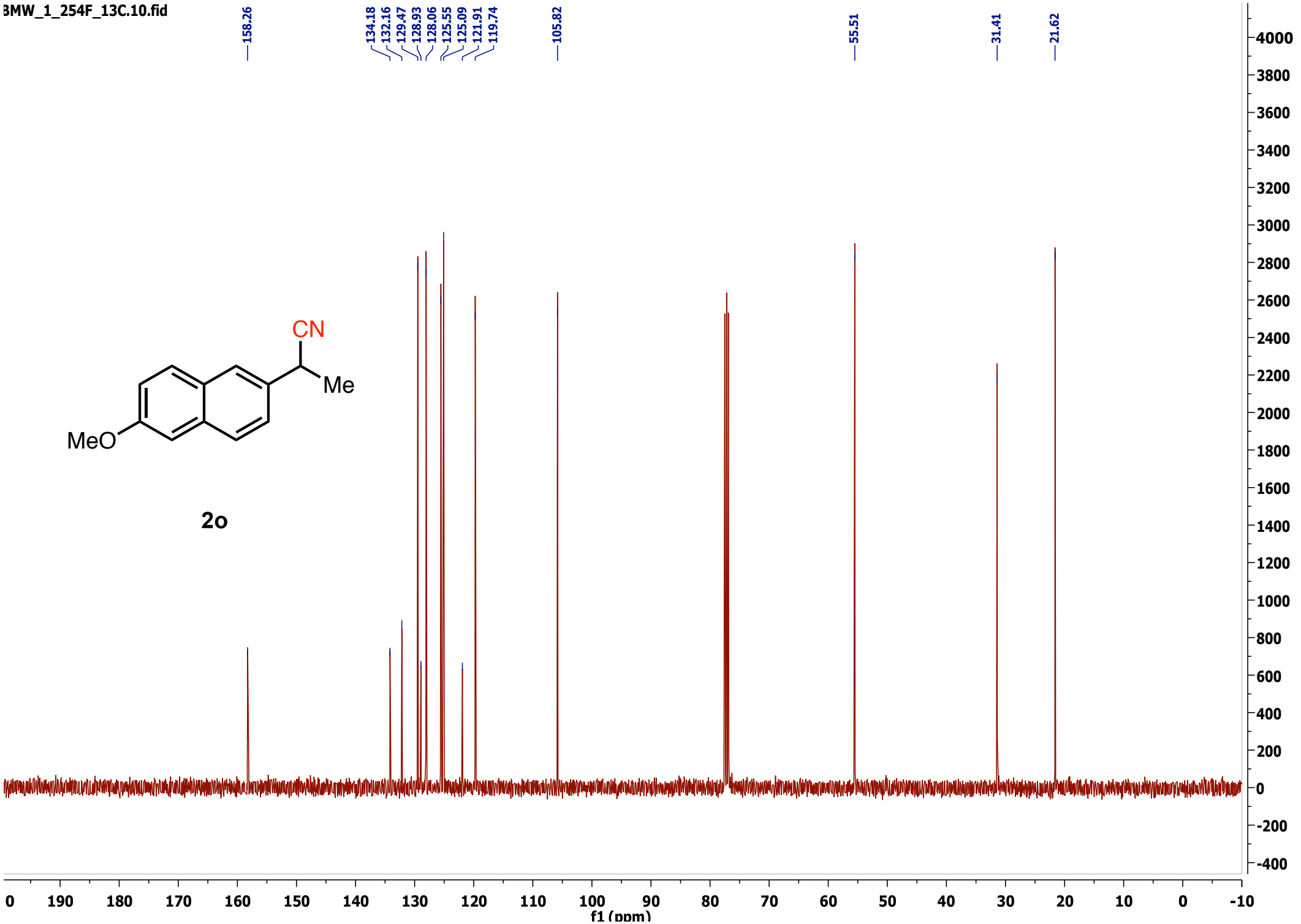

BMW_1_130_13C.10.fid
120.18
80.59
46.21
43.56
28.53
28.45
28.08
27.55
23.23
CN
N
Boc
2m
f1 (ppm)


RYL946_n2_1H.10.fid
7.47
7.45
7.38
7.36
7.34
7.31
7.29
7.27
5.44
3.08
S
CN
2n
4.05
4.03
1.99
1.00
1.99
f1 (ppm)

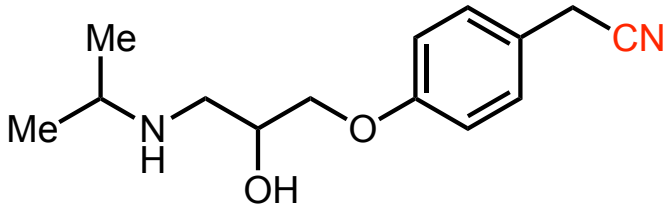
RYL946_n2_13C.10.fid




BMW_1_254F_1H.10.fid
7.77
7.75
7.72
7.40
7.40
7.38
7.38
7.20
7.20
7.18
7.17
7.14
7.13
4.06
4.04
4.02
4.00
3.93
1.72
1.70
CN
Me
MeO
2o
3.02
1.00
0.99
0.99
1.00
3.07
3.10
f1 (ppm)


BMW_1_254F_13C.10.fid
158.26
134.18
132.16
129.47
128.93
128.06
125.55
125.09
121.91
119.74
105.82
55.51
31.41
21.62
CN
Me
MeO
2o
f1 (ppm)

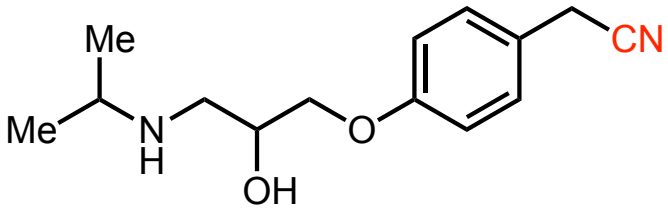
BMW_1_233_1H.10.fid



2q

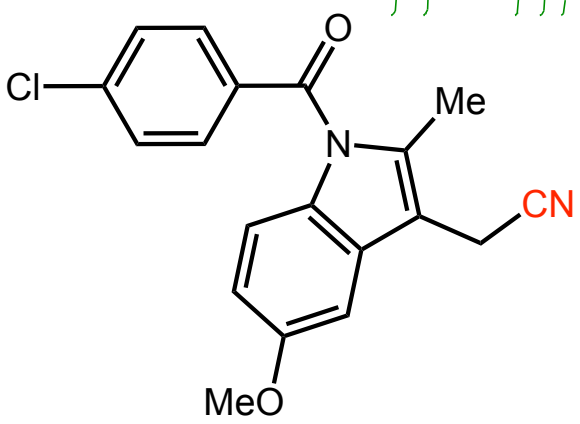
f1 (ppm)

BMW_1_233_13C.10.fid



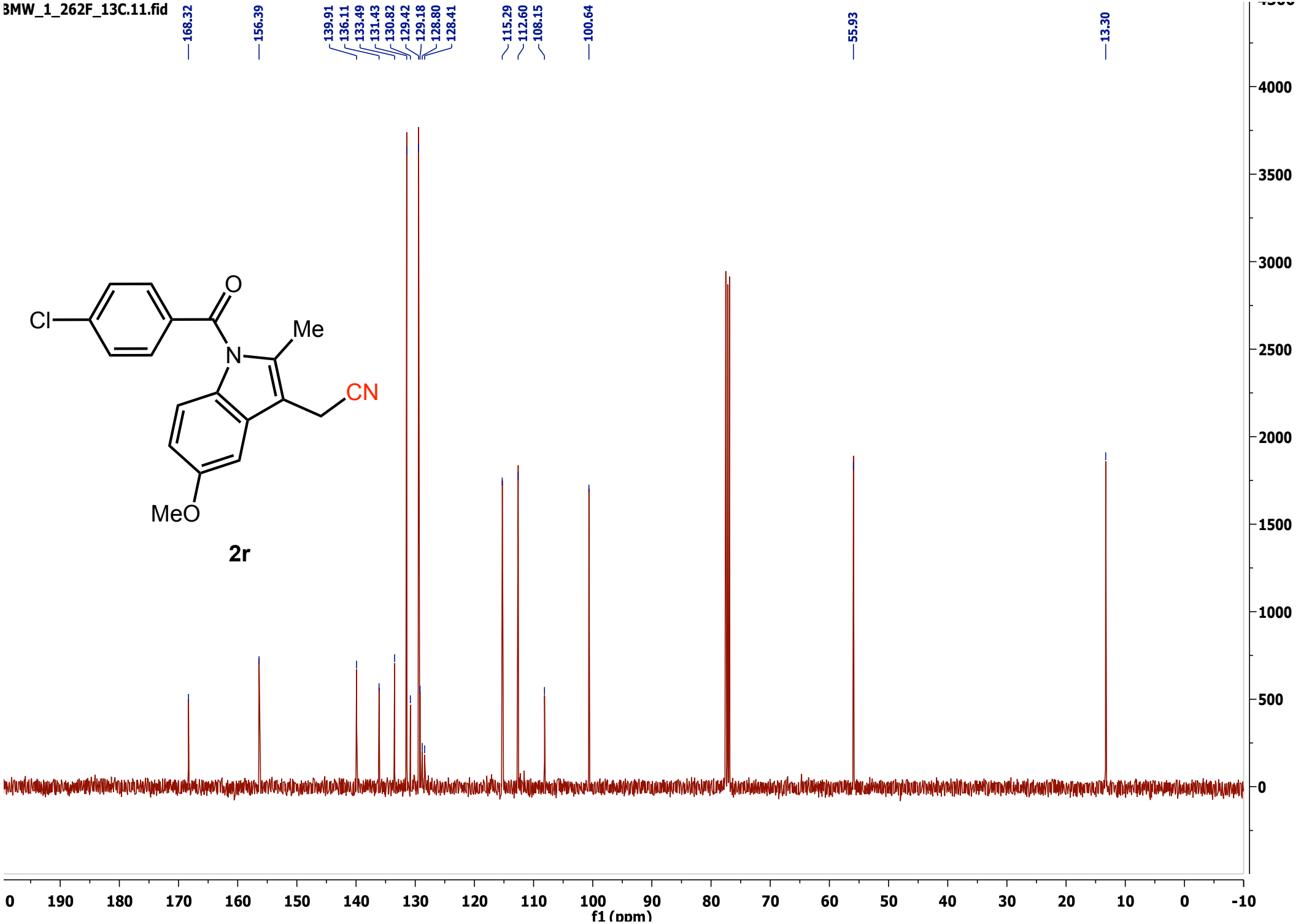
2q

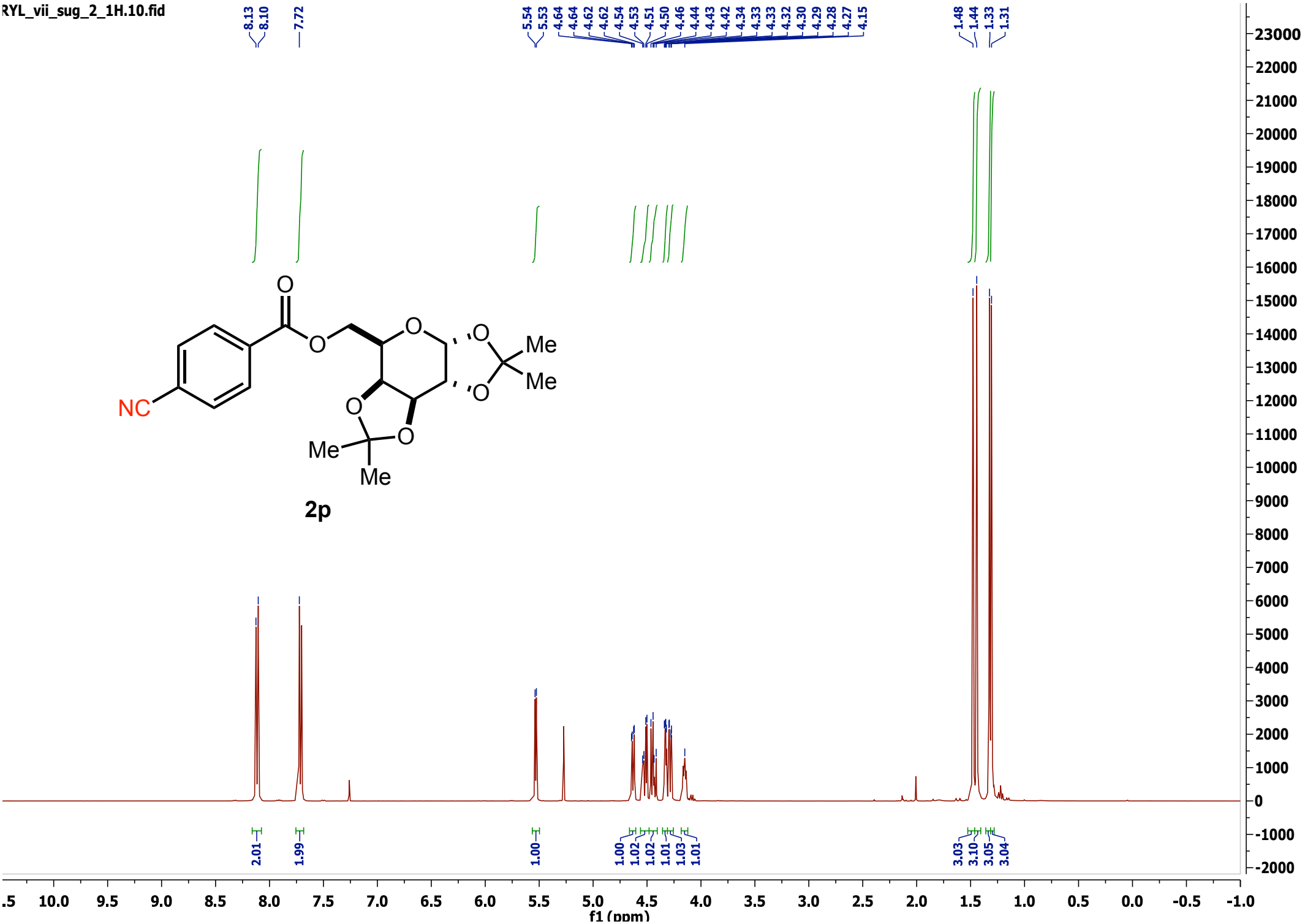
BMW_1_262F_1H.10.fid

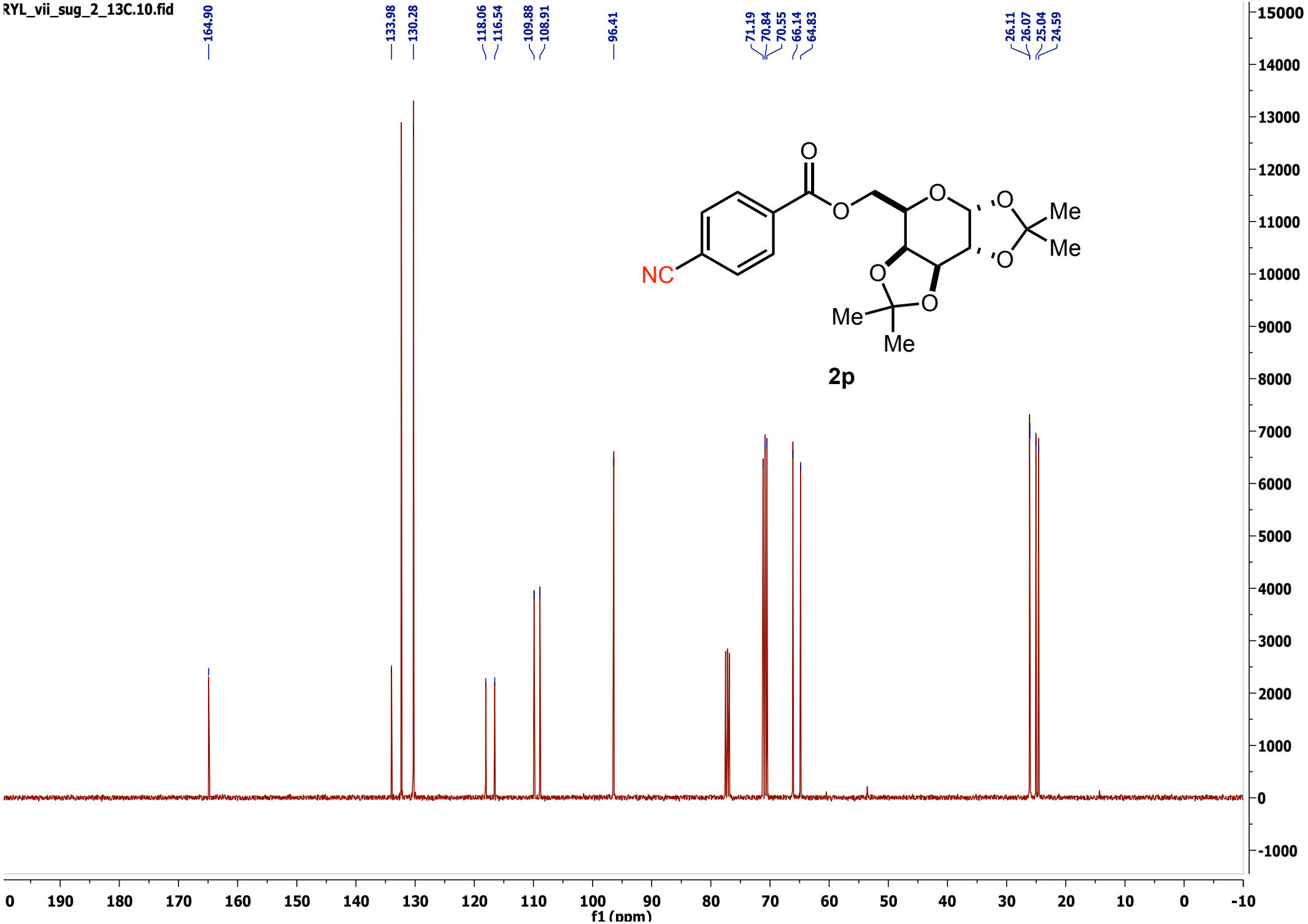


2r

f1 (ppm)


BMW_1_262F_13C.11.fid
168.32
156.39
139.91
136.11
133.49
131.43
130.82
129.42
129.18
128.80
128.41
115.29
112.60
108.15
100.64
55.93
13.30
Cl
O
N
Me
CN
MeO
2r
4000
3500
3000
2500
2000
1500
1000
500
0
0 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


RYL_vii_sug_2_1H.10.fid
8.13
8.10
7.72
5.54
5.53
4.64
4.64
4.62
4.62
4.54
4.53
4.51
4.50
4.46
4.44
4.43
4.42
4.34
4.33
4.33
4.32
4.30
4.29
4.28
4.27
4.15
1.48
1.44
1.33
1.31
NC
O
O
O
O
O
O
Me
Me
Me
Me
2p
2.01
1.99
1.00
1.00
1.02
1.02
1.01
1.03
1.01
3.03
3.10
3.05
3.04
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


RYL_vii_sug_2_13C.10.fid
164.90
133.98
130.28
118.06
116.54
109.88
108.91
96.41
71.19
70.84
70.55
66.14
64.83
26.11
26.07
25.04
24.59
NC
O
O
O
O
O
O
O
Me
Me
Me
Me
2p
f1 (ppm)